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THE

PHYSICAL REVIEW.

LIGHT ABSORPTION AND FLUORESCENCE.

By E. C. C. Baly.

Synopsis.

Quantitative Relationships between the Vibration Frequencies of Molecules as Shown by Absorption, Fluorescence, or Phosphorescence Bands; Comparison of Theoretical Predictions with Experimental Results.—In an earlier paper the author predicted the frequencies of the absorption bands of naphthalene in the infra-red from the ultra-violet absorption and fluorescence. The later experimental data of Stang did not confirm the predicted values, and this fact caused the proposer of the theory to present in the present paper an explanation of the discrepancy and to give a generalization of the original theory.

The lack of agreement was due to two causes: (*a*) the theory was dependent upon the alleged unsatisfactory nature of the conceptions of Bjerrum and of Krüger, which relate respectively to molecular rotational velocities and to molecular precessional velocities, and (*b*) the experimental data upon which the hypotheses were based were incomplete. From a critical study of the frequencies exhibited by sulphur dioxide and by water vapor, the following *general law of molecular frequencies* is deduced, namely: the frequencies truly characteristic of a molecule are multiples of the least common multiple of the frequencies of the atoms it contains, and the subgroups are due to intra-molecular frequencies, that is, the least common multiples of groups of atoms within the molecule.

Fluorescence of Naphthalene.—The subgroup series in the fluorescence band of this substance has a constant frequency difference of 1.4136×10^{13}, which is now shown to be an intramolecular frequency instead of a true molecular frequency, as assumed in the earlier paper. This conclusion is justified by the chemical constitution of the naphthalene molecule and the excellent agreement between the predicted frequencies and the experimental data obtained by Coblentz for ethylene.

Fluorescence of Uranyl Salts.—In further confirmation of the hypothesis of intramolecular frequencies, the author discusses (with tabulated data) the experimental results of Nichols and Merritt on the fluorescence bands of uranyl ammonium chloride and of uranyl nitrate trihydrate.

IN a recent paper in the Physical Review,[1] Stang has published some very interesting and important measurements of the infra-red absorption bands exhibited by naphthalene and a few of its derivatives. One of the objects was to test the validity of my theory of the quantitative

[1] Phys. Rev., 9, p. 542, 1917.

relationship between the various vibration frequencies possessed by molecules and evidenced by them as absorption, fluorescence, or phosphorescence bands.[1] I ventured to foretell the frequencies of the absorption bands of naphthalene in the infra-red from the ultra-violet fluorescence and absorption, and at first sight it might be a little disappointing to find that the values obtained by Stang do not agree with my calculations.

On the other hand since the date of my paper it has been found possible to obtain much more information as to the relationships which exist between the various frequencies shown by a given compound. This has been rendered possible by a study of the absorption spectrum of sulphur dioxide, for which very accurate determinations of the vibration frequencies in the infra-red and ultra-violet have been made. It may be noted here that my prediction of the infra-red spectrum of naphthalene was based entirely on the Bjerrum conception of molecular rotational frequencies and there is now little doubt that this theory together with the Krüger[2] conception of molecular precessional velocities is not capable of explaining the relationships that have been observed.

In order to find an explanation of the apparent discrepancy in the case of naphthalene the complete relationship found in sulphur dioxide may be very briefly detailed.[3] Every single frequency that has been observed with this gas can be expressed in terms of three fundamental frequencies, 2.4531×10^{11}, 8.19×10^{11}, and 1.296×10^{12}. Of these 2.4531×10^{11} is characteristic of oxygen, and 8.19×10^{11} and 1.296×10^{12} are characteristic of sulphur, since the infra-red bands of oxygen can be expressed in terms of the first, whilst those of sulphur and hydrogen sulphide can be expressed in terms of the last two. I have already shown in previous papers that the least common multiple principle forms the basis of molecular frequencies, and the least common multiple of the three fundamental frequencies given above is 2.89299×10^{12}. This number multiplied by 10, 12, 14, 18, 26, and 33 gives the exact central frequencies of all the absorption bands which have yet been observed for sulphur dioxide in the infra-red. Then again of these absorption bands the one with the central frequency $2.89299 \times 14 \times 10^{12}$ has the greatest intensity, and this central frequency multiplied by 25 gives the exact central frequency of the less refrangible absorption band in the ultra-violet, the center of the more refrangible band not having yet been observed.

Now it is well known that the central frequency of an absorption band is a true molecular frequency since it is the only frequency which persists

[1] Astrophys. Journal, 42, p. 4, 1915.

[2] Ann. der Physik, 50, p. 346, 51, p. 450, 1916.

[3] Baly and Garrett, Phil. Mag., 31, p. 152, 1916.

when the substance is cooled to a very low temperature. The important conclusion therefore is reached that the frequencies truly characteristic of a molecule are multiples of the least common multiple of the frequencies of the atoms it contains.

Again the ultra-violet absorption band of sulphur dioxide consists of a series of subgroups symmetrically arranged round a central subgroup, and further each subgroup consists of a central line with a series of lines symmetrically arranged round it. Considering first the central lines of the subgroups it has been found that these form a series with constant frequency difference, these constant frequency differences being the least common multiples of two only of the atomic frequencies. Thus the central lines of the subgroups in the less refrangible ultra-violet band of sulphur dioxide form a series with constant frequency difference of 6.69696×10^{12} which is the least common multiple of 8.19×10^{11} and 2.4531×10^{11}. In the more refrangible band the constant frequency difference between the sub-groups is 1.05972×10^{13}, which is the least common multiple of 8.19×10^{11} and 1.296×10^{12}. Lastly the individual lines within each sub-group also form a series with constant frequency difference, and in this case the constant frequency difference is equal to one of the atomic frequencies. Thus in each subgroup of the less refrangible ultra-violet band the component lines form a series with the constant frequency difference 8.19×10^{11}.

It may be concluded from this that whilst the true molecular frequencies are multiples of the least common multiple of the frequencies of the atoms it contains, the subgroups are due to intra-molecular frequencies, that is the least common multiples of groups of atoms within the molecule. In case this be thought too important a deduction to make from one set of observations it may be stated that exactly the same relationship has been found in the case of the frequencies exhibited by water vapor. Obviously if 2.4531×10^{11} is a characteristic frequency of oxygen it must form one of the bases of the molecular frequency system of water. Then we have the two intramolecular frequencies of water, 7.5×10^{11} and 1.7301×10^{12}, which have been called the molecular rotational velocities of the water molecule. These intramolecular frequencies will be the least common multiples of two out of the three fundamental atomic frequencies active in the water molecule, one of these being 2.4531×10^{11}. The other two atomic frequencies are at once found to be 1.0635×10^{11} and 2.1159×10^{11}. The least common multiple of all three is 6.1326×10^{12} and this number multiplied by 8 gives the exact central frequency of the great absorption band of water at 6.115 μ, and when multiplied by 16 the exact central frequency of the

band at 3.0575 μ. Further, by assuming an exactly analogous relationship with sulphur dioxide I have calculated the individual lines in the absorption band at 6.115 μ and these agree extraordinarily closely with the actual measurements made by Sleator.[1]

Apart from the somewhat obvious conflict between these relationships now established and the Bjerrum and Krüger theories, they have a very material significance as regards the infra-red absorption of naphthalene. The subgroup series in the fluorescence band of naphthalene shows a constant frequency difference of 1.4136×10^{13} ($1/\lambda = 47.12$). In my original paper I assumed on the basis of the Bjerrum theory that this was the molecular rotational frequency and that naphthalene should exhibit absorption bands in the infra-red with central frequencies of $1.4136 \times 10^{13} \times 1, 2, 3, 4, 5$, etc., or wave-lengths 21.22 μ, 10.61 μ, 7.07 μ, 5.31 μ, 4.24 μ, etc. The experience now gained from sulphur dioxide and water shows that this frequency is not a molecular frequency at all, but an intra-molecular frequency due to a group of atoms within the naphthalene molecule, and need not necessarily appear in the infra-red absorption spectrum of naphthalene.

Now if this frequency, 1.4136×10^{13}, is an intra-molecular frequency of naphthalene it must clearly be a true molecular frequency of a group of atoms in the naphthalene molecule. There are two very obvious groups in this molecule, namely the benzene grouping and the olefine linking. It is therefore to be expected that either benzene or the olefines should show as true molecular frequency the intra-molecular frequency of naphthalene, 1.4136×10^{13}. In other words one or the other should show absorption bands with centers at 21.22 μ, 10.61 μ, 7.07 μ, 5.31 μ, 4.24 μ, and further, since the intensity of the effect in naphthalene decreases with the size of the multiple of 1.4136×10^{13}, the intensity of these bands should be greatest at 21.22 μ and should decrease with decreasing wave-length in the series.

It is well known that benzene does not show any of these bands but the infra-red absorption spectrum of ethylene has been observed by Coblentz between 13 μ and 3 μ.[2] He finds absorption bands with centers at 10.5 μ, 6.98 μ, 5.30 μ, and 4.32 μ, *these being the only bands observed between these limits*. The agreement is very striking and moreover with the thickness of ethylene used the amount of light absorbed was 98, 81, 47, and 14 per cent. respectively. The sixth member of the series was not detected owing doubtless to its weakness and also to the presence of the band at 3.28 μ which does not belong to this series. Coblentz'

[1] Astrophys. Journal, 48, p. 125, 1918.

[2] Carnegie Inst. Publ., No. 35, 1905. Attention may be drawn to the remarkable similarity between the infra-red absorption spectra of the members of a homologous series.

measurements did not extend beyond 13 μ and consequently he did not observe the very strong band which must exist at 21.22 μ.

It may fairly be claimed that this establishes the reality of these intramolecular frequencies. Possibly also I may be excused for the error I made in assuming the complete validity of the Bjerrum theory which led me to believe that 1.4136×10^{13} was a true molecular frequency of naphthalene.

Reference may also be made here to the very interesting results obtained by Nichols and Merritt[1] upon the fluorescence spectra of uranyl

TABLE I.

	1/λ	Diff.
1st group	1469.7	20.2 = 1 × 20.2
	1489.9	center
	1507.1	17.2 = 1 × 17.2
	1521.8	31.9 = 2 × 15.95
Average difference, 17.32		
2d group	1538.2	35.2 = 2 × 17.6
	1553.3	20.1 = 1 × 20.1
	1573.4	center
	1588.9	15.5 = 1 × 15.5
	1605.1	31.7 = 2 × 15.85
Average difference, 17.25		
3d group	1621.5	34.4 = 2 × 17.2
	1638.9	17.0 = 1 × 17.0
	1655.9	center
	1672.8	16.9 = 1 × 16.9
	1689.4	33.5 = 2 × 16.75
Average difference, 16.97		
4th group	1705.9	32.8 = 2 × 16.4
	1719.9	18.8 = 1 × 18.8
	1738.7	center
	1755.4	16.7 = 1 × 16.7
	1772.2	33.5 = 2 × 16.75
Average difference, 16.97		
5th group	1789.1	31.4 = 2 × 15.7
	1802.8	17.7 = 1 × 17.7
	1820.5	center
	1839.4	18.9 = 1 × 18.9
	1856.0	35.5 = 2 × 17.75
Average difference, 17.25		
Central group	1871.2	32.8 = 2 × 16.4
	1886.1	17.9 = 1 × 17.9
	1904.0	center
	1922.6	18.6 = 1 × 18.6
	1939.2	35.2 = 2 × 17.6
Average difference, 17.42		
7th group	1955.3	30.9 = 2 × 15.45
	1970.1	16.1 = 1 × 16.1
	1986.2	center
	2005.7	19.5 = 1 × 19.5
	2022.6	36.4 = 2 × 18.2
Average difference, 17.15		
8th group	2038.3	32.7 = 2 × 16.35
	2053.3	17.7 = 1 × 17.7
	2071.0	center
	2089.0	18.0 = 1 × 18.0
	2105.9	34.9 = 2 × 17.45
	2121.5	50.5 = 3 × 16.83
Average difference, 17.09		

Mean of all the subdifferences, 17.16

salts which would seem to conform in a very remarkable way to the general theory of absorption and fluorescence. The diagram given by these authors for the fluorescence bands of uranyl ammonium chloride represents an almost perfect example of the symmetrical distribution of the

[1] PHYS. REV., 6, p. 360, 1915.

TABLE II.

	1/λ	Diff.
1st group.....	1629.2	14.7 = 2 × 7.35
	1637.2	6.7 = 1 × 6.7
	1643.9	center
	1667.2	23.3 = 3 × 7.77
	1677.0	33.1 = 5 × 6.62

Average difference, 7.07

2d group.....	1686.1	43.1 = 6 × 7.2
	1699.8	29.4 = 4 × 7.35
	1704.2	25.0 = 3 × 8.3
	1715.2	14.0 = 2 × 7.0
	1722.8	6.4 = 1 × 6.4
	1729.2	center
	1741.8	12.6 = 2 × 6.3
	1748.6	18.4 = 3 × 6.1
	1755.0	25.8 = 4 × 6.45
	1765.0	35.8 = 5 × 7.16

Average difference, 7.02

3d group.....	1772.0	44.1 = 6 × 7.35
	1778.7	37.4 = 5 × 7.48
	1785.9	30.2 = 4 × 7.55
	1791.8	24.3 = 3 × 8.1
	1802.1	14.0 = 2 × 7.0
	1808.7	7.4 = 1 × 7.4
	1816.1	center
	1821.3	5.2 = 1 × 5.2
	1828.1	12.0 = 2 × 6.0
	1835.3	19.2 = 3 × 6.4
	1842.4	26.3 = 4 × 6.6
	1851.5	35.4 = 5 × 7.1

Average difference, 7.10

4th group.....	1858.7	43.3 = 6 × 7.2
	1865.1	37.9 = 6 × 7.6
	1873.0	30.0 = 4 × 7.5
	1877.4	25.6 = 3 × 8.5
	1889.0	14.0 = 2 × 7.0
	1895.3	7.7 = 1 × 7.7
	1903.0	center
	1908.9	5.9 = 1 × 5.9
	1915.9	12.9 = 2 × 6.45
	1923.3	20.3 = 3 × 6.8
	1930.1	27.1 = 4 × 6.8
	1938.8	35.8 = 5 × 7.18

Average difference, 7.24

5th group.....	1945.7	44.2 = 6 × 7.37
	1952.9	37.0 = 5 × 7.4
	1959.1	30.8 = 4 × 7.7
	1965.3	24.6 = 3 × 8.2
	1976.4	13.5 = 2 × 6.75
	1982.3	7.6 = 1 × 7.6
	1989.9	center
	1995.9	6.0 = 1 × 6.0
	2002.1	12.2 = 2 × 6.1
	2009.8	19.9 = 3 × 6.6
	2017.4	27.5 = 4 × 6.9
	2025.0	35.1 = 5 × 7.0

Average difference, 7.18

6th group.....	2033.2	43.1 = 6 × 7.2
	2046.8	29.5 = 4 × 7.4
	2051.0	25.3 = 3 × 8.4
	2064.3	12.0 = 2 × 6.0
	2070.3	6.3 = 1 × 6.3
	2076.3	center
	2083.8	7.5 = 1 × 7.5
	2089.7	13.4 = 2 × 6.7
	2103.5	27.2 = 4 × 6.8
	2112.7	36.4 = 5 × 7.3

Average difference, 7.17

Mean of the subdifferences, 7.13

subsidiary intramolecular frequencies round the central and most strongly marked molecular frequency. According to my theory this band consists of a central group with five groups on the red side and two groups on the blue side. Each group at ordinary temperatures consists of five subgroups symmetrically arranged round a central subgroup, and at lower temperatures these subgroups are still further resolved. This

arrangement is very similar indeed to that already described for sulphur dioxide. Two constant wave number differences are present, namely 83.20 between the centers of the groups and a secondary difference of 17.1 between the subgroups of each group. This secondary difference is shown in the following table and is calculated in each instance from the central band of the group, the average for each group being calculated from the total number of times the interval occurs.

The central wave number of the band or the molecular wave number is 1904 and this therefore should be a multiple of the wave number of an important band in the infra-red spectrum of uranyl ammonium chloride.

A second fact of importance is the change in the wave number difference in the absorption band between the heads of the groups, this difference being about 71 instead of 83.2 in the fluorescence band. This is exactly similar to the case of sulphur dioxide as stated above, and it shows that the effective intramolecular or atomic frequencies are different according to the condition of the molecular force field of the salt.

The grouping is still better shown in the fluorescence band of uranyl nitrate trihydrate which has more recently been examined.[1] This band may be arranged in six groups, the maximum number of subgroups in each group being 12. The secondary differences are shown in Table II.

In the case of the above group the principal intramolecular wave number is 86.8 while the secondary wave number is 7.13. It is interesting to note that the principal intramolecular wave number for the absorption band of uranyl nitrate trihydrate is just 10 times the secondary wave number for the fluorescence band.

THE UNIVERSITY,
LIVERPOOL.

[1] Nichols and Merritt, PHYS. REV., 9. p. 113, 1917.

NOTE ON THE ADSORPTION OF NITROGEN AND OXYGEN BY CHARCOAL.

BY ROBERT E. WILSON.

SYNOPSIS.

Discussion of Previously Published Results on the Adsorption of Oxygen, Nitrogen, and their Mixtures in Activated Charcoal at Liquid Air Temperatures.—This paper is based on experimental data recently set forth in this REVIEW, "Studies in the Adsorption of Gases by Charcoal, II.," by Lemon and Blodgett.[1]

Definite Relationship between Mols of Oxygen, Nitrogen, or Mixtures Adsorbed.—Attention is called to the surprising fact, hitherto not mentioned, that the number of mols of oxygen adsorbed to any given final pressure is almost exactly 1.30 times the number of mols of nitrogen adsorbed to the same final pressure. The pressure *vs.* volume adsorbed curve for pure oxygen and for mixtures of oxygen and nitrogen can, therefore, be very accurately calculated from the results obtained with nitrogen alone. Furthermore, it is also possible to reproduce all the curves representing the *rate* of adsorption from the results obtained with nitrogen alone.

Bearing of Foregoing Relationship on Theory of Adsorption; Nature of Forces by which Gas Molecules are Held.—By a mathematical treatment of the foregoing data, it can be demonstrated that neither Langmuir's one layer adsorption theory (which undoubtedly applies to that portion of the gas held with the greatest tenacity) nor the "capillary condensation theory" (which applies to loosely held liquid in capillaries of moderate size) are applicable to the intermediate range of pressures covered by Lemon and Blodgett's data. Their results can, however, be explained on the basis of the following hypotheses: (1) the ratio of the molecular volume of adsorbed nitrogen to that of adsorbed oxygen is the same as for the free liquids (1.31 at − 192° C.); (2) the gases are held in layers several molecules deep primarily by the attractive force of the charcoal surface; (3) the stray field around oxygen and nitrogen molecules is substantially the same at any given distance.

SOME very interesting data have recently been published in this journal by Lemon and others, on the adsorption of various gases by charcoal. In the second of that series of articles Lemon and Blodgett[1] describe the results of a series of experiments on the adsorption of oxygen and nitrogen and mixtures of the two by charcoal. In these experiments various amounts of oxygen or nitrogen or their mixtures were suddenly admitted to a chamber containing an activated and previously evacuated specimen of cocoanut-shell charcoal at liquid air temperature. The rate of decrease in pressure and the final equilibrium pressure attained by each mixture was recorded and presented in tabular or graphic form in the article. On the basis of the results therein detailed it was con-

[1] PHYSICAL REVIEW, XIV., 5, November, 1919.

cluded that oxygen and nitrogen are not adsorbed independently, but no attempt was made to point out any definite relationship between the adsorption of the two gases and their mixtures.

A close study of the data therein presented brings to light, however, an extremely interesting fact which seems to have considerable bearing on the question of the mechanism of adsorption. Although at first sight there appears to be no simple relationship between the results obtained on the adsorption of oxygen and of nitrogen, as a matter of fact if the simple assumption is made that one mol of nitrogen is in every way equivalent to 1.30 mols of oxygen, it is possible to calculate not only the results obtained with pure oxygen, but also those for various mixtures of the two gases, by using merely the data obtained with pure nitrogen.

Since the observed points on the three curves do not exactly correspond,

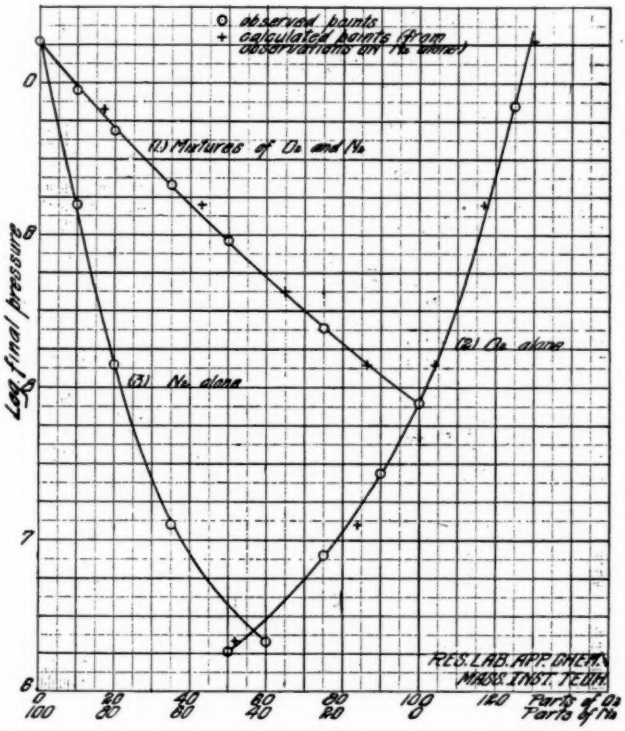

Fig. 1.

Agreement between calculated and observed values of final pressures of oxygen and mixtures of oxygen and nitrogen absorbed in charcoal.

the best way to test the above assumption is to calculate from one nitrogen observation to a point which should lie on the smooth curve connecting the observed points for oxygen or the mixtures. These smooth curves

are obtained by plotting the log of the final pressure against the parts of gas adsorbed (see Fig. 1 corresponding to Fig. 5 of the original article).

The method of making these calculations is as follows: If one mol of nitrogen is exactly equivalent to 1.30 mols of oxygen, then 130 parts O_2 should give the same log final p as that given by 100 parts N_2 (0.270). Similarly the observed pressures for 80 parts N_2 should exactly correspond to $1.3 \times 80 = 104$ parts O_2. By calculating the five observed nitrogen points over to their oxygen equivalent in this manner, the five crosses on the oxygen curve were obtained. As will be observed, these agree remarkably closely with the smooth curve drawn through the circles which represent the observed points on the oxygen curve. In a similar manner, it is possible to calculate points on the mixture curve, using only the observed points for nitrogen; and it will be observed that again the agreement between the calculated points and the observed curve is excellent.

Another way to show the agreement between the calculated and observed values is to calculate values corresponding to each observed point for oxygen or the mixtures from the corresponding points on the smooth curve connecting the nitrogen observations. The agreement thus obtained is shown in Table I.

TABLE I.

Parts O_2.	Parts N_2.	Should = Parts N_2.	Log p Calculated.	Log p Observed.	Difference.
125	0	96.2	9.86	9.85	−0.01
100	0	76.8	7.88	7.90	+0.02
90	0	69.2	7.38	7.43	+0.05
75	0	57.7	6.84	6.89	+0.05
50	0	38.5	6.30	6.26	−0.04
75	25	82.7	8.39	8.38	−0.01
50	50	88.5	8.98	8.97	−0.01
35	65	91.9	9.36	9.33	−0.03
20	80	95.4	9.74	9.69	−0.05
10	90	97.7	9.98	9.95	−0.03

Small deviations, of course, occur in plotting a smooth curve through any series of points, so that the "calculated" values themselves cannot be considered especially precise even if the theory were exact.

It is thus possible from a single series of observations on different amounts of nitrogen to calculate very accurately the corresponding curves for oxygen, and for mixtures of oxygen and nitrogen, merely by assuming that one mol of nitrogen is exactly equivalent to 1.30 mols of

oxygen. Furthermore, even the curves for the rate of adsorption may be reproduced very closely by making the same assumption. For example, the rate curve for 80 parts N_2 should, by the above method of calculation, lie between the curve for 100 parts O_2 (= 76.8 parts N_2) and that for 75 parts O_2 and 25 parts N_2 (= 82.7 parts N_2); and as a matter of fact this is found to be the case when the three curves (taken from Figs. 2 and 4 of original article) are plotted on the same coördinates

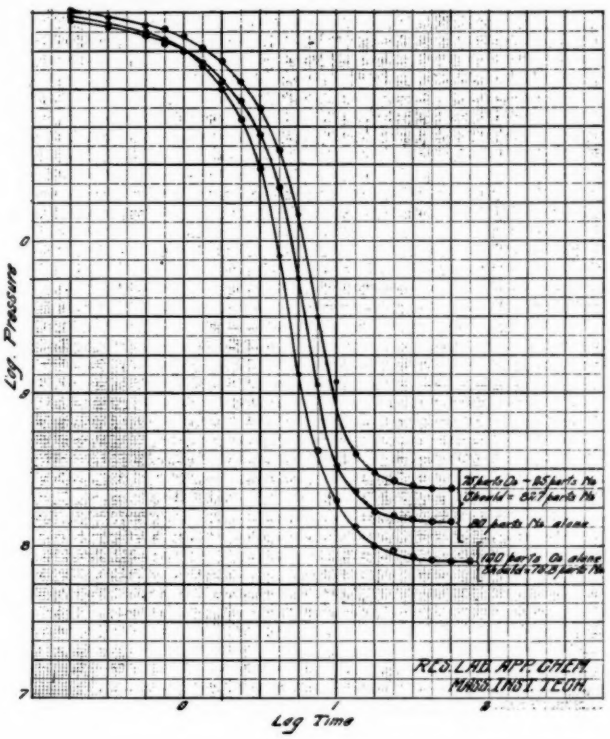

Fig. 2.

Correspondence between rates of adsorption of pure gases and mixtures.

as in Fig. 2 of this article. By similar interpolation it is possible to approximate any other rate curve for the results for nitrogen alone.

This remarkable parallelism between the adsorption of oxygen and nitrogen, extending as it does over a variation in final pressures of nearly ten thousand-fold, should certainly throw some light on the mechanism of the adsorption of these two gases. As in any case where adsorption takes place inside capillaries of unknown size and number, there is a wide variety of assumptions which can be made to explain any set of known facts providing a sufficient number of variables are introduced. It is the purpose of this note, however, to call attention to an extremely

simple assumption which seems to explain adequately all the foregoing facts.

An important question which should be considered at the outset is whether the gases are adsorbed in films one layer deep, as Langmuir has demonstrated to be the case in certain examples of adsorption, or whether they are several layers deep, possibly completely filling the smaller capillaries. In this particular case both the amount of gas adsorbed and the pressure which it exerts definitely support the latter view. Hulett and others have shown that well-activated charcoal holds very considerable amounts of oxygen and nitrogen even in a good vacuum at high temperatures. This firmly held gas would certainly seem to be that which is adsorbed in a layer one molecule deep. Since its pressure is inappreciable even at temperatures of 200–300° C., it would certainly not be measurable at liquid air temperatures. Furthermore, as the temperature is lowered and approaches the condensing point of the gases, the amounts of gas adsorbed increase greatly—certainly to more than ten-fold those held at the higher temperatures. It would appear, therefore, that only a small fraction of the gas adsorbed in the experiments described by Lemon and Blodgett could be held in the layer one molecule deep, and that the measurably high vapor pressures recorded were produced by the last portions of the gas which were held but loosely in layers possibly 8 or 10 molecules distant from the charcoal surface.

As a first step, then, it seems reasonable to assume that the above mentioned definite ratio between the number of mols of the different gases adsorbed to any given final pressure, might correspond to the relative molecular volumes occupied by the adsorbed gases, which at liquid air temperatures would presumably approximate the liquid state. The best data on the densities of liquid oxygen and nitrogen seem to be those of Baly and Donnan[1] who give the following figures for the density of liquid oxygen as a function of the absolute temperature in the vicinity of its boiling point. (The figures are rounded.)

$$dO_2 = 1.249 - 0.0048(T - 68),$$

$$dN_2 = 0.854 - 0.0048(T - 68).$$

Assuming liquid air temperature to be − 192° C., this gives the densities as 1.187 and 0.792 respectively, which corresponds to relative *molecular* volumes of 1.310 for N_2 to 1 for O_2. It will be observed that this is remarkably close to the ratio of 1.30 determined from the adsorption measurements. Certainly the agreement seems too close to be considered a coincidence, in view of the relationship which might reasonably be expected to exist between these two quantities.

[1] J. Chem. Soc., 81, 911.

These simple and apparently reasonable results do not, however, fit in well with the customary explanation of the absorption of gases in capillaries—the "capillary condensation" theory. This theory assumes that adsorption in a porous material such as charcoal is almost entirely (except for the first layer of molecules) due to the known fact that the vapor pressure of a liquid inside a fine capillary, the walls of which are wet by the liquid, decreases greatly with the decrease in the diameter of the capillary. This law may be expressed quantitatively as follows:[1]

$$ln\frac{p}{P} = -\frac{2\lambda}{RT\rho r}$$

or in more convenient form for calculations:

$$\log_{10}\frac{P}{p} = \frac{2.085\lambda V}{10^2 Td}.$$

Where	Values at −192° C.	
	For O_2.	For N_2.
P = vapor pressure of free liquid	25.2 cm.[2]	114 cm.[1]
p = " " of absorbed liquid		
λ = surface tension in dynes/cm.	15.73[3]	8.27[2]
V = molal volume of liquid	26.95	35.30
T = absolute temp. in °C.	81.1	81.1
d = diameter of capillaries		

Using these figures, if the vapor pressure lowering in the case under consideration is due to capillary condensation the pressure of condensed oxygen should be:

$$\log pO_2 = 1.401 - \frac{10.90}{10^8 d}$$

and for nitrogen

$$\log pN_2 = 2.056 - \frac{7.50}{10^8 d},$$

where d is the diameter of the *largest* capillaries in which the condensed liquid is held (since this part of the liquid is responsible for the observed final pressures).

From the foregoing it should be possible to calculate the diameter of the capillaries which would correspond to different final pressures of oxygen or nitrogen, and then find, by referring to Fig. 1, the number of

[1] For derivation see R. v. Helmholtz, Wied. Ann., 27, 508, 1886.

[2] Baly, Phil. Mag., 49, 517, 1900.

[3] Values for − 193° C. by Baly and Donnan, Trans. Chem. Soc., 81, 907, 1902.

parts of oxygen or nitrogen which were actually adsorbed between these pressure limits. Table II. summarizes the results of such calculations.

TABLE II.

Diameter of Capillaries Centimeters.	Calc. log p of O_2.	Calc. log p of N_2.	Parts of O_2 Condensed.	Parts of N_2 Condensed.	Ratio.
$0-2\times10^{-8}$...	$-\infty$ to -4.05	$-\infty$ to -1.69	35	82	0.23
$2-3\times10^{-8}$...	-4.05 to -2.23	-1.69 to $-.44$	62	12	5.2
$3-4\times10^{-8}$...	-2.23 to -1.33	$-.44$ to $+.18$	15	5	3.0

In other words, a given set of capillaries ($0-2\times10^{-8}$ cm.) appear to take up more than four times as much oxygen as nitrogen, but the next largest group of capillaries ($2-3\times10^{-8}$) condense over five times as much nitrogen as oxygen! Furthermore, practically all of the gas adsorbed would appear to be held in capillaries whose diameters lie between the narrow limits of 1 and 5×10^{-8} cm. Since these absurd results follow necessarily from the mathematical application of the capillary condensation theory, it must be concluded that the theory is not applicable for such small capillaries, although its validity seems to be established for the larger capillaries where the lowering of vapor pressure is only very slight.

Since neither the one-layer adsorption theory nor the capillary condensation theory appears to apply to the intermediate range of pressures covered by Lemon and Blodgett's work, it seems desirable to develop some new conceptions to explain the surprising results pointed out previously in this paper. If, for example, it be assumed that the primary reason for the low vapor pressure is the attraction of the charcoal surface for the gases, the vapor pressure of the adsorbed oxygen and nitrogen would then depend only upon their distance from the charcoal surfaces and upon their own stray fields of force. If the *stray fields* of force of the two kinds of molecules are *equal* at a given distance, and the *relative volumes* of the condensed gases are as *1 to 1.30*, as seems probable from the density data, then it would follow as a necessary conclusion that a given sample of charcoal at any definite temperature and any final pressure would hold 1.30 times as many mols of oxygen as of nitrogen. Since this is in precise accord with the observed facts, and the assumptions are not only simple but justified by other known facts, this would seem to be a very satisfactory working hypothesis in the light of the information at present available.

It may at first sight seem unlikely that oxygen and nitrogen should have equal stray fields at any given distance from their center, in view

of the fact that their boiling points differ by about 12° C. This divergence could, however, be entirely accounted for by the fact that the molecules of oxygen come closer together in the liquid state and hence the attractive forces of these molecules for one another would be somewhat greater, even though the stray field at any given distance were exactly the same as that for nitrogen.

It must, of course, be admitted that certain other more complicated assumptions might be made to explain the same facts; for example, the capillary condensation theory, or indeed almost any theory, could be explained by assuming that the ratio of the molal volumes of the adsorbed gases varied widely from the 1.30 which seems most reasonable, coupled with certain very arbitrary assumptions as to the gradation in the sizes of the pores in the particular sample of charcoal used. The writer has followed several of these more complicated hypotheses through to their logical conclusion without finding one of enough value to justify its detailed presentation as a possible substitute for the foregoing theory, at least in the light of the data at present available.

In conclusion, although Langmuir's theory of one layer adsorption

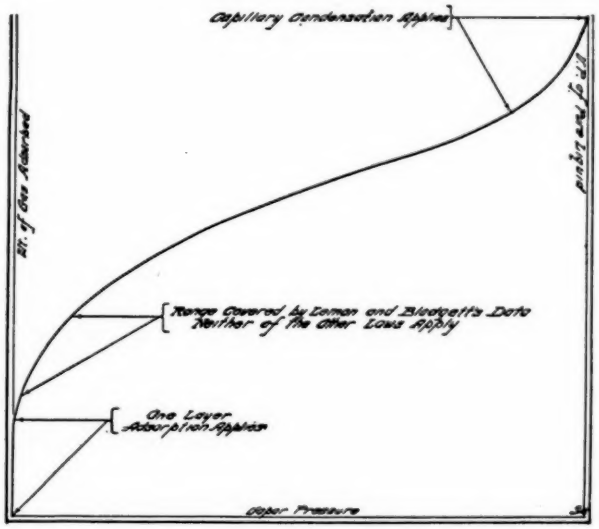

Fig. 3.

appears to be well established for the small amounts of gas which are held with extreme tenacity on a solid surface, and although the capillary condensation theory seems to adequately explain the slightly depressed vapor pressures in capillaries of moderate size, there is a wide intermediate range of adsorption covered by Lemon and Blodgett's work in which

neither theory seems to be satisfactory. The range over which different types of adsorption appear to hold are shown roughly in Fig. 3, which represents a typical adsorption curve for charcoal over the whole range of volumes and pressures.[1]

To explain the results obtained in this intermediate region, the following hypotheses are therefore suggested:

1. The ratio between the molecular volumes of adsorbed oxygen and nitrogen is very close to the ratio between the molecular volumes of the free liquids at the same temperature (about 1 to 1.30).

2. The stray field around oxygen molecules is substantially the same as that around nitrogen molecules at any given distance.

3. The gases are held primarily by the attractive force of the charcoal surface, in layers more than one molecule deep, and not by capillary condensation.

These hypotheses adequately explain the known facts, and require no assumptions whatever as to the gradation in the sizes of the pores in the charcoal, or as to the functional relationship between the distance from the charcoal surface and its attractive force.

It would be extremely interesting to compare the similar results obtained by varying the gases, the charcoal, or the temperature from that prevailing in these experiments. Data obtained along these lines should serve either to definitely verify or discredit the foregoing hypotheses.

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[1] See article by the writer and others in J. Ind. Eng. Chem., 11, 420, 1919.

ON ELECTROMAGNETIC MOMENTUM.

By H. A. Wilson.

Synopsis.

Fundamental relations involving electromagnetic momentum.—A simple way of deducing the force per unit volume acting in the electromagnetic field is given which makes clear the nature of the force in terms of elementary ideas. The well-known relation between the *flux of energy* and the momentum in the field suggests that all momentum is due to energy flux. Starting with this assumption a simple relation is obtained between the momentum, energy and *velocity of the center of mass* of any system. This relation when applied to a single particle leads to the same relations between the longitudinal and transverse *masses* and the velocity as have been deduced from the principle of *relativity*. Several particular examples are discussed.

Relations of matter and ether to stresses.—It is argued that since the electromagnetic field has momentum, energy and is subject to *gravitational attraction* it therefore possesses all the essential properties of matter and that therefore the *stresses* in the field should be regarded as acting through the field and on it in the same way that stresses act in ordinary matter. When there is a resultant force on a space containing matter the force is supposed to act on the matter and not on the ether in the space and the motion of matter and the stresses in it are not supposed to act on the ether or to tend to set it in motion. We should therefore regard the stresses in the electromagnetic field as acting on the field and not on the ether. There is therefore no more reason to suppose that the ether is set in motion in an electromagnetic field than there is for supposing that it is set in motion by the stresses in or the motion of ordinary matter.

The transmission of energy and momentum in the field.—This is considered from the point of view indicated. The theory is similar to that given by E. Cunningham who however regards the motion in the field as motion of the ether. Cunningham also supposes that the velocity is always equal to the velocity of light. I have not adopted this assumption but instead I suppose that the direction of the velocity of the field coincides with the direction of the momentum in the field. In this way the *flux of energy* in the field is explained as partly due to the working of the stresses in the field and partly to *convection of energy* with the moving field. Several examples are discussed. Finally some results are mentioned which follow from the idea that energy is subject to *gravitational attraction.*

THE hypothesis that momentum can exist in an electromagnetic field or in the ether was first put forward by J. J. Thomson in 1893 and was afterwards developed by Poincaré and Abraham. It now forms part of the generally accepted electromagnetic theory.

If F denotes the total force on the electricity inside a closed surface S then it may be shown that

$$F = \int_S (\text{Maxwell's Stresses})\, dS - \frac{1}{c}\int_\sigma \frac{d}{dt}\,[d\cdot h]d\sigma,$$

where σ denotes the volume enclosed by S; c is the velocity of light; d denotes the electric and h the magnetic intensity. Thus it appears that the resultant of the stresses acting across the surface S is greater than the total force acting on the electricity inside S by an amount

$$\frac{1}{c}\int_\sigma \frac{d}{dt}[d\cdot h]d\sigma.$$

This integral has therefore been said to represent a mechanical force acting on the ether inside S which it is natural to suppose is made up of forces $(d/dt)[d\cdot h]/c$ per unit volume. The nature of this mechanical force may be made clear in the following way.

According to Maxwell's theory a displacement current $(\dot{d})$ produces the same magnetic field as an equal conduction current. The force on a current in a magnetic field is undoubtedly due to the interaction of the magnetic field of the current with the external field so that we should expect a force on a displacement current equal to that on a conduction current. We should therefore expect a force equal to $[\dot{d}\cdot h]/c$ per unit volume on the displacement current $\dot{d}$ when in a magnetic field of strength h since the force on a conduction current of density i is $[i\cdot h]/c$ per unit volume.

A varying magnetic field may be said to produce a magnetic displacement current $\dot{h}$ which produces an electric field opposite in direction but otherwise precisely analogous to the magnetic field due to a current. We should therefore expect a force on a magnetic displacement current when in an electric field of amount $[d\cdot\dot{h}]/c$ per unit volume.

The total force per unit volume is therefore

$$[\dot{d}\cdot h]/c + [d\cdot\dot{h}]/c = \frac{1}{c}\frac{d}{dt}[d\cdot h]$$

which agrees with the usual result. Since force is equal to momentum communicated per unit time the existence of this force $(1/c)(d/dt)[d\cdot h]$ has therefore led to the view that there is in the electromagnetic field or in the ether an amount of mechanical momentum equal to $[d\cdot h]/c$ per unit volume.

J. J. Thomson supposes this momentum to be the momentum of moving tubes of electric force which on his theory give rise to the magnetic field.

It appears that in the electromagnetic field there is momentum $[d\cdot h]/c$ associated with a flux of energy $c[d\cdot h]$. A similar result[1] has been deduced from the principle of relativity namely that the convection of energy by a moving body implies an amount of momentum equal to the product of the energy and velocity divided by c^2.

[1] Relativity and the Electron Theory, E. Cunningham, p. 80.

It seems probable therefore that a flux of energy is always associated with an amount of momentum equal to the flux divided by c^2. It is natural therefore to regard this momentum as due to inertia of the energy and to regard all momentum as due to a flux of energy. Consider any material system moving in any manner with reference to coördinates x, y, z. Let E denote the energy density at any point in the system and let the flux of energy per unit area per unit time be denoted by F. Then if $\bar{x}$ denotes the x coördinate of the center of mass of the energy in the system we have

$$\bar{x} = \frac{\int xEdS}{\int EdS},$$

where dS denotes an element of volume. Differentiating this with respect to the time t and writing $\mathcal{E}$ for $\int EdS$ this gives

$$\mathcal{E}\dot{\bar{x}} = \int x\dot{E}dS.$$

Now $\dot{E} = -$ div F, so that

$$\mathcal{E}\dot{\bar{x}} = -\int x \text{ div } FdS.$$

If the integration is extended over a volume so large that F is zero over the surface enclosing it this gives

$$\mathcal{E}\dot{\bar{x}} = \int F_x dS,$$

where F_x denotes the x component of F. If now we suppose that a flux of energy F_x in the x direction is associated with x momentum per unit volume equal to F_x/c^2 we get

$$M_x = \frac{1}{c^2}\int F_x dS,$$

where M_x denotes the total momentum of the system, due to energy flux, in the x direction. Hence

$$\mathcal{E}\dot{\bar{x}} = M_x c^2.$$

Thus it appears that the total momentum of the system due to energy flux is equal to the total energy in the system multiplied by the velocity of the center of mass of the energy in the system and divided by c^2. If all momentum is due to energy flux then the center of mass of the energy will coincide with the center of mass of the system.

As an example consider a condenser consisting of two large parallel plates kept at a fixed distance s apart by means of insulating blocks. Let the electric intensity between the plates be d and let the condenser be moving with a velocity v in a direction perpendicular to the planes of its plates.

The energy density between the plates is $d^2/2$ and the flux of energy between the plates is zero since there is no magnetic field. The plates attract each other with a force $d^2/2$ per unit area so that there will be a pressure in the blocks separating the plates equal to $Ad^2/2$, where A is the area of each plate. There is therefore a flux of energy in the blocks equal to $Ad^2v/2$ so that if we take v to be along the x direction

$$\int F_x dS = \frac{Ad^2vs}{2}.$$

The momentum due to the flux of energy is therefore

$$Ad^2vs/2c^2,$$

which is equal to the electrical energy $Asd^2/2$ multiplied by v/c^2.

Charging the condenser therefore increases its momentum in a direction perpendicular to its planes although there is no flow of electromagnetic energy in this case. We may observe that between the plates there is a tension $d^2/2$ and a density of energy $d^2/2$ which produces a flow due to convection $vd^2/2$ so that the total energy flux is zero whatever the value of v in agreement with the value of $c[d \cdot h]$ in this case.

Now consider the case when the condenser moves in a direction parallel to the planes of its plates. When v is very small compared with c we get a magnetic field between the plates equal to vd/c and perpendicular to v and d. There is therefore a flow of energy between the plates equal to $c[d \cdot h] = vd^2$ which gives for the electromagnetic momentum $Asvd^2/c^2$. There is also a tension in the plates in the direction of v equal to $\frac{1}{2}sd^2(1 - v^2/c^2)$ which gives a flow of energy per unit length in the plates equal to $\frac{1}{2}vsd^2(1 - v^2/c^2)$ in the opposite direction to v. The momentum corresponding to this is $-\frac{1}{2}Asvd^2(1 - v^2/c^2)/c^2$ so that the total momentum is

$$\frac{Asvd^2}{c^2} - \frac{1}{2}\frac{Asvd^2}{c^2}(1 - v^2/c^2) = \frac{Asvd^2}{2c^2}(1 + v^2/c^2).$$

The electromagnetic energy is equal to

$$\mathcal{E} = \frac{As}{2}(d^2 + h^2) = \frac{Asvd^2}{2}\left(1 + \frac{v^2}{c^2}\right),$$

so that

$$\frac{\mathcal{E}v}{c^2} = \frac{Asvd^2}{2c^2}(1 + v^2/c^2),$$

which agrees with the value just found for the momentum as was to be expected.

As another example consider the Lorentz electron, which when at rest is a thin hollow sphere of electricity of radius a and charge e. When

moving with velocity v in the x direction it contracts into a spheroid of revolution with axes

$$a\sqrt{1 - v^2/c^2}, \qquad a \text{ and } a.$$

The electromagnetic momentum of the Lorentz electron calculated by integrating $[d \cdot h]/c$ is equal to

$$\frac{e^2}{6\pi ac^2}\beta(1 - \beta^2)^{-\frac{1}{2}}$$

where $\beta = v/c$. The sum of the electric and magnetic energies is equal to

$$\frac{e^2}{\pi a}\frac{3 + \beta^2}{24(1 - \beta^2)^{\frac{1}{2}}}.$$

Thus the electromagnetic momentum is not equal to the electromagnetic energy multiplied by v/c^2.

In order to maintain the electricity in equilibrium it is necessary, as was shown by Poincaré, to suppose that it is pulled inwards by an internal stress the x component of which must be equal to $e^2/32\pi^2a^4$. The work done by this stress when v is increased from zero to c is equal to the stress multiplied by the volume $\frac{4}{3}\pi a^3$ of the sphere so that we may suppose that there is energy inside the sphere of amount $e^2/32\pi^2a^4$ per unit volume.

The flux of energy inside the sphere is therefore zero since there is a tension in the direction of motion equal to the energy density. The internal energy therefore does not contribute anything to the momentum. The total energy is therefore

$$\frac{e^2}{\pi a}\frac{3 + \beta^2}{24(1 - \beta^2)^{\frac{1}{2}}} + \frac{e^2}{32\pi^2a^4}\frac{4}{3}\pi a^3(1 - \beta^2)^{\frac{1}{2}} = \frac{e^2}{6\pi a(1 - \beta^2)^{\frac{1}{2}}}.$$

Multiplying this by $v/c^2 = \beta/c$ we get

$$\frac{e^2\beta}{6\pi ac}(1 - \beta^2)^{-\frac{1}{2}},$$

which is equal to the momentum. It appears that when the energy inside the sphere is taken into account the momentum of the Lorentz electron is equal to its total energy multiplied by v/c^2 as it should be.

If a force F acts on a particle moving in the direction of the force then $F\delta t = \delta M$ and $Fv\delta t = \delta\mathcal{E}$ so that $v\delta M = \delta\mathcal{E}$ which with $M = \mathcal{E}v/c^2$ gives $\mathcal{E} = \mathcal{E}_0(1 - v^2/c^2)^{-\frac{1}{2}}$ where $\mathcal{E}_0$ is the energy of the particle when $v = 0$. This result is a well-known deduction from the principle of relativity. The momentum of the particle due to energy flux is therefore given by

$$M = \mathcal{E}_0 vc^{-2}(1 - v^2/c^2)^{-\frac{1}{2}}.$$

The transverse mass m' of the particle due to energy flux is given by

$$m' = M/v = \mathcal{E}_0 c^{-2}(1 - v^2/c^2)^{-\frac{1}{2}}$$

and the longitudinal mass m'' due to energy flux by

$$m'' = dM/dv = \mathcal{E}_0 c^{-2}(1 - v^2/c^2)^{-\frac{3}{2}}.$$

The ratio of the transverse mass m' to the longitudinal mass m'' is therefore

$$\frac{m'}{m''} = 1 - v^2/c^2.$$

These results will be true for a particle of any kind. They will therefore be true for any of the different types of electrons which have been proposed. It follows that the measurements of e/m for electrons for different values of v, made by Kaufmann, Bucherer and others do not really enable us to decide in favor of any particular type. The results obtained agree with the view that momentum is due to energy flux but if this view is correct than the variation of m with v is the same for any sort of particle whether composed of electricity or not.

If all momentum is due to energy flux then we should expect all energy to be subject to gravitational attraction. This is confirmed by the recent discovery of the deflection of light by the gravitational field of the sun.

The force represented by $(1/c)(d/dt)[d \cdot h]$ has usually been regarded as a force acting on the ether. Thus H. A. Lorentz says that in consequence of the existence of this force we must either regard the ether as having so great a density that its motion due to this force is negligible or else we must regard Maxwell's stresses as imaginary ones, merely auxiliary mathematical quantities not representing real stresses.[1]

In ordinary mechanics we deal with stresses acting in material bodies which are supposed to move through the ether without setting it in motion. For example when power is transmitted from one pulley to another by means of a belt we have a flux of energy along the belt which is partly a convection of kinetic energy equal to $\frac{1}{2}\rho v^2 \times v$ where ρ is the density and v the velocity of the material of the belt and partly a transmission of energy due to work done by the tension T in the belt equal to $-Tv$ per unit area of cross-section of the belt.

Now the ultimate particles of the matter composing the belt are believed to be some sort of ethereal modifications which move through the unmodified ether without setting it in motion presumably by a process of growing in front and fading away behind. Thus in ordinary

[1] Theory of Electrons, p. 31.

mechanics forces act on ethereal modifications and energy is transmitted by stresses existing in such modifications when they move through the ether. When there is a resultant force on a portion of space we do not regard this force as tending to set the ether in the space in motion but only as tending to produce a motion of the ethereal modification or matter there present.

The electromagnetic field is like matter in that it is believed to be some sort of modification of the ether. Like matter it can move through the ether and possesses energy and momentum and is subject to gravitational attraction. It seems therefore that we ought to regard the force $(1/c)(d/dt)[d \cdot h]$ as acting not on the ether but on the ethereal modification present that is on the electromagnetic field. If we adopt this view then we may regard the ether as always at rest and the Maxwell's stresses as acting through the field so that when these stresses give a resultant force on a portion of space then this force tends to produce a motion of the ethereal modifications present in the portion of space whether the modifications present consist of matter, electricity or only an electromagnetic field. This way of regarding the matter is consistent with our conceptions of the nature of matter and the transmission of energy through ordinary matter in motion. Force, as we know it, is something which tends to change the motion through the ether of an ethereal modification without setting the ether itself in motion. The motion of the ethereal modification is really a process of change of state and not motion at all but for convenience may be referred to as a motion through the ether. A force does work on the moving matter although there is really only change of state and no motion. This involves no contradiction because in the definition of work nothing is said about the nature of the process by which the matter acted on by the force moves.

If the observed effects of force are really only changes of state in a stagnant ether then there is no reason to suppose that the ether can ever be set in motion. We may still speak of matter as moving through the ether provided we understand that the expression merely refers to the change of position and not to the nature of the process by which the change takes place.

If we regard the force $(1/c)(d/dt)[d \cdot h]$ as acting on the electromagnetic field then we must regard the momentum $[d \cdot h]/c$ as due to a motion in the field. We have seen that this momentum can be regarded as due to the flux of energy so that it is natural to conclude that the flux of energy is the motion in the field to which the momentum is due.

Now the flux of energy may be made up of two parts, a convection of the energy present per unit volume through the ether with a velocity v

that is $\frac{1}{2}(d^2 + h^2)v$ and a flux due to work done by stress. The velocity v may be taken to be in the direction of the momentum and the energy flux that is along the direction of the vector $[d \cdot h]$. The velocity v is the velocity with which the field moves through the ether. The process by which this motion takes place being the same as the process by which matter moves through the ether. Presumably a process of growing in front and fading away behind by changes of state in a stagnant ether. In the case of light waves moving with velocity c such a process is merely wave motion in the usual sense. It may be objected that we ought not on this view to regard any energy as moving by a process of convection but it must be understood that the process of convection is of the same nature as the convection of energy by a moving particle which also moves by a process of change of state. Thus what we call convection is really very much of the same nature as wave motion but it is convenient to express what happens in the electromagnetic field in terms of ideas derived from experience with matter in bulk. The statement that some of the energy in the field moves by a process of convection is intended to be understood as meaning convection like that by a moving particle which moves by changes of state in a stagnant ether.

In the same way the flux of momentum may be due partly to convection of momentum and partly to stress in the field. The Maxwell stresses of course represent the total flow of momentum.

At a point in an electromagnetic field suppose the momentum $[d \cdot h]/c$ is directed along the x axis and let d be along the y axis and let the angle between d and h be θ so that $h_y = h \cos \theta$ and $h_z = h \sin \theta$.

Consider a small plane area α and let the direction cosines of its normal be l, m, n. Let X_n', Y_n', Z_n' be the components of the stresses acting across α. Then if q be written for $[d \cdot h]/c$ the flux of energy along the normal to α is lqc^2 so that we have

$$- X_n'v + Elv = lqc^2, \tag{1}$$

where v denotes the velocity of the field which is along x and E denotes the energy density $\frac{1}{2}(d^2 + h^2)$.

The flux of x momentum across α will be given by

$$X_n' - qlv = X_n, \tag{2}$$

where X_n denotes the x component of the Maxwell's stress across α.

The fluxes of y and z momentum will be given by $Y_n' = Y_n$ and $Z_n' = Z_n$ simply because all the momentum in the field is x momentum so that there is no convection of y or z momentum.

Now when d is along y and $h_z = 0$ as we are supposing to be the case

we have

$$X_n = -\tfrac{1}{2}l(d^2 + h^2) = -lE.$$

Substituting this value of X_n in (2) we get

$$X_n' = qlv - lE.$$

Hence (1) becomes

$$2Ev - qv^2 = qc^2,$$

which gives

$$v = \frac{E}{q} \pm \sqrt{\frac{E^2}{q^2} - c^2}.$$

One root is less than c and the other greater. Presumably the one less than c should be taken.

A calculation similar in principle to the above has been published previously by E. Cunningham who however regards the velocity v as that of the ether, whereas I prefer to regard it as the velocity of the electromagnetic field through the ether.

In the case of light waves we have $E = d^2$ and $q = d^2/c$ so that $v = c$. This means that in light waves the field moves along through the ether with the velocity c as was to be expected. Cunningham however concludes that in light waves the ether moves along with the light with the velocity c of light so that the waves are at rest relative to the ether.

Cunningham also does not assume that the velocity is along the direction of $[d \cdot h]$ but he assumes that the resultant velocity of the ether is always equal to c. It seems to me to be much more reasonable to assume that the velocity is along the direction of $[d \cdot h]$. For all the momentum is in this direction and we should naturally expect the velocity of the field to be in the same direction as the momentum.

We have

$$\begin{aligned} X_n' &= qlv + X_n \\ &= l(qv - E) \\ &= -l\sqrt{E^2 - q^2c^2}, \end{aligned}$$

so that there is a pressure in the x direction. In the case of light waves travelling along x if we take d along y as before then h will be along z so that $\theta = 90°$, $E = d^2$, $q = d^2/c$ and $h = d$. Hence

$$\begin{aligned} X_n' &= -l\sqrt{E^2 - q^2c^2} = 0, \\ Y_n' &= Y_n = 0, \\ Z_n' &= Z_n = 0. \end{aligned}$$

Thus in light there is no stress, as was shown by Cunningham, but simply the field moving through the ether carrying its energy and momentum with it.

This result at first sight appears to be inconsistent with the wave theory of light but the paradox is only apparent. The motion of the field through the ether must be supposed to take place by a process of growing in front and fading away behind of some form of modification of the ether. The modification being the presence of electric and magnetic fields. This is clearly the same thing as is usually meant by the wave theory. The calculation given above shows that the flux of energy in the electromagnetic field can be explained on mechanical principles as due to convection and the working of stresses in the moving field. By mechanical principles we mean the ordinary mechanical processes which are supposed to take place in moving matter. The electromagnetic theory is more fundamental than our ideas of mechanical processes so that when electromagnetic theory is interpreted mechanically we have to use the ideas of convection and motion through the ether derived from experience with matter in bulk instead of the more fundamental idea of wave motion or motion by a process of change of state in a stagnant medium.

The equation

$$v = \frac{E}{q} \pm \sqrt{\frac{E^2}{q^2} - c^2}$$

in the case when d and h are at right angles reduces to either $v = ch/d$ or $v = cd/h$. The proper value to take is presumably the one which is less than c.

When d and h are at right angles and h less than d the relation between v, h and d is the same as in the theory of J. J. Thomson, in which h is supposed to be due to the motion of the electric tubes of force. We may remark that J. J. Thomson's theory is especially successful when applied to cases in which d and h are at right angles and h less than d.

It appears that the flow of energy in an electromagnetic field can be explained on mechanical principles. The energy is transmitted partly by convection due to motion of the field through the ether and partly by the working of stresses in the moving field. The ether remains at rest and in fact does not enter into consideration at all. The momentum in the field is regarded as associated with the energy flux and the velocity of the field is along the direction of the momentum and the energy flux.

It is interesting to consider the flux of energy along a tube of energy flow in a steady field. Such a tube may be bounded by two neighboring equipotential surfaces of electrostatic potential and two equipotential surfaces of magnetic potential. If we consider a short length of such a tube then it will, in general, be curved. The flow of energy along it

and the associated momentum therefore change in direction as the field moves along the tube. There must therefore be a force on the tube at right angles to its length sufficient to produce the change in the direction of the momentum. The Maxwell stresses in a steady field give no resultant force on any element of volume free from charge. The stresses perpendicular to the tube are the Maxwell stresses but along the tube the true stress X' is less than the Maxwell stress X. We have seen that $X' = qv + X = qv - E$. The pressure in the direction of the tube of energy flow is therefore less than the Maxwell pressure by qv. There will therefore be a transverse force on the tube equal to qv/R per unit volume, where R is the radius of curvature of the tube. This force will be directed towards the center of curvature. This force is of just the right amount required to keep the flux of energy along the tube for it is equal to the momentum times the velocity divided by R just as the force required to keep a particle of mass m on a circular path is mv^2/R.

Consider again the case of a moving charged parallel plate condenser. First suppose it is moving in a direction perpendicular to its plates with velocity V. The energy flux between the plates and the velocity of the field are both zero. Thus the plate ahead continually generates new electric field behind it as it moves along and the plate behind continually absorbs the energy from the field. The energy flows from the back plate to the front plate through the insulating supports. The velocity of the field relative to the plates is $-V$ so that the field goes into one plate and comes out of the other.

If the condenser moves parallel to its plates with velocity V then $h = Vd/c$ so that the velocity v of the field is equal to

$$v = \frac{E}{q} - \sqrt{\frac{E^2}{q^2} - c^2} = V.$$

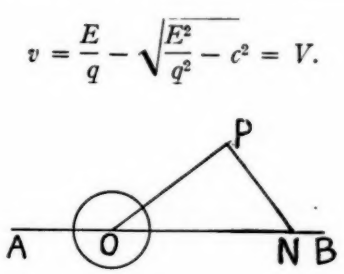

Fig. 1.

Thus the field moves along with the plates which seems a reasonable conclusion.

Now consider the case of a charged sphere moving with a small velocity V along a straight line AB. Let the center of the sphere be at O (Fig. 1)

at a point P if $OP = r$ and $P\hat{O}B = \theta$ we have

$$d = \frac{e}{4\pi r^2}, \qquad h = \frac{eV \sin \theta}{4\pi r^2 c},$$

so that the velocity of the field v is given by $v = ch/d = V \sin \theta$ and is directed along PN. Thus if ON represents V then PN represents v.

The velocity of the field relative to the sphere will be got by adding $-V$ to v so that it will be represented by PO. That is, the field to an observer on the sphere will appear to be coming in towards the center of the sphere with a velocity $V \cos \theta$. If θ is greater than $\pi/2$ the relative velocity is along the radius away from the sphere. Thus the field is absorbed by the sphere in front of it and emitted behind. The velocity of the field relative to the sphere at the surface of the sphere is equal and opposite to the velocity of the surface along the normal.

Next consider the case of a condenser consisting of two long concentric cylinders with radii a and b. Let the charge on the inside cylinder be e per cm. of length along the axis and suppose that the condenser is moving with a velocity V in the direction of its axis. There is then a convection current eV carried by the inner cylinder and a current $-eV$ carried by the outer cylinder. The magnetic intensity between the cylinders will be equal to $eV/2\pi rc$ at a distance r from the axis. The radial electric intensity will be equal to $e/2\pi r$. The velocity of the field is therefore, since d and h are perpendicular to each other and $h < d$, given by

$$v = c \times \frac{eV}{2\pi rc} \times \frac{2\pi r}{e} = V,$$

so that the field moves along with the condenser as was to be expected. The velocity v is equal to C/e, where $C = eV$ denotes the current. If ϕ denotes the potential difference between the cylinders then

$$e = 2\pi\phi / \log b/a$$

so that

$$v = \frac{C}{2\pi\phi} \log b/a.$$

In the case of two concentric cylindrical conductors with a current C flowing along the inner one and a current $-C$ along the outer one the magnetic and electric fields between the cylinders are the same as in the case of the moving condensers so the velocity of the field will be the same. The flow of energy between the cylinders is in either case equal to $C\phi$ so that the momentum in the field is equal to $C\phi/c^2$ per unit length along the axis. If V is small so that the magnetic energy can be neglected compared with the electric then since the electrostatic energy per cm.

is equal to $\frac{1}{2}e\phi$ the flow of energy due to convection is equal to $\frac{1}{2}e\phi V$ or $\frac{1}{2}C\phi$ so that half the energy is convected and half transmitted by the working of the stress in the field.

In the case of the condenser there is a backward flow of energy in the cylinders equal to $\frac{1}{2}e\phi V$ due to the tension along them so that the total flux of energy along the axis is $\frac{1}{2}e\phi V$ as it evidently must be.

In the case of the concentric conductors at rest there is no backward flow and the total flow is $C\phi$. In this case the velocity of the center of mass of the energy is evidently $lC\phi/\frac{1}{2}e\phi l = 2C/e$ where l is the length of the conductors so that the momentum due to energy flux is given by

$$\frac{E\bar{v}}{c^2} = \frac{2C}{e} \times \frac{l\frac{1}{2}\phi e}{c^2} = \frac{C\phi l}{c^2}$$

or $C\phi/c^2$ per unit length as before. In the case of the condenser the momentum is only $\frac{1}{2}C\phi l/c^2$ because half the energy flows back along the cylinders.

When the current is first started in the conductors they will receive an impulse in the negative direction due to the generation of this momentum in the field. This impulse is due to the field existing at the end where the current is started before it gets to the other end. The pressure due to the field therefore acts at one end for a short time before it is balanced by the equal pressure at the other end.

An analogous case in mechanics can be easily imagined. Suppose we have a long closed box with a machine gun in the box at one end. If the gun starts firing along the box the box will receive an impulse which will last until the bullets begin to strike the other end. The box will therefore move backwards if it is free to move as long as the gun continues to fire and will be stopped shortly after the gun stops firing.

Consider now the case of a condenser consisting of two long concentric cylinders when a uniform magnetic field is generated parallel to the axis. The momentum per unit volume between the cylinders in this case is $he/2\pi rc$ so that the total angular momentum in the field per unit length along the axis is $(b^2 - a^2)he/2c$ where b and a are the radii of the cylinders. While the field is being generated the cylinders are acted on by a couple due to the induced electric intensity which gives them angular momentum equal but opposite to that generated in the field.

This case offers a possibility of testing the theory of electromagnetic momentum experimentally. A cylindrical condenser with its axis vertical could be suspended by a fibre so that it could rotate. The outside cylinder could be closed at each end and the inner one given a static charge. The condenser could be suspended inside a solenoid to produce

the magnetic field. The condenser should be deflected when the magnetic field is produced. If however the force $(1/c)(d/dt)[d \cdot h]$ is transmitted through the field to the charges on the cylinders instead of generating momentum in the field then no deflection would be obtained. The effect to be expected in such an experiment is very small but might possibly be detected with a well designed apparatus.

If we regard all momentum as due to energy flux then we might expect all energy to be subject to gravitational attraction. This idea has been confirmed by the recent discovery of the deflection of light when passing by the sun. The momentum M in the light is finite so that the transverse mass which is equal at any velocity to M/v is also finite but the longitudinal mass is equal to $M(1 - v^2/c^2)^{-1}$ and so should be infinite for light. This means that a force acting on light in the direction of motion should not increase the velocity of the light but should merely increase the momentum and energy in the same proportion so that $v = Mc^2/\mathcal{E}$ remains constant. We should therefore expect the gravitational force of the sun to change the direction of light but not its velocity. Of course Einstein's theory gives a change of velocity but it is based on the idea that the gravitational field distorts space.

If energy is subject to gravitation then various effects must exist which are unfortunately probably too small to be detected. For example suppose electrical energy is transmitted from a battery through a wire of small resistance to a higher level where it is converted into heat in a resistance R. Let C denote the current and E the electromotive force of the battery. Then we have

$$EC = C^2R + C^2Rgh/c^2,$$

where g denotes the acceleration due to gravity and h the difference of level. Thus the resistance will apparently be $R(1 + gh/c^2)$ instead of R. If $h = 10{,}000$ meters the increase in R is about one in 10^{12}.

Again in a circuit composed of two metals if one junction is at a higher level than the other we should expect a small electromotive force even when the two junctions are at the same temperature. This electromotive force should be approximately equal to Pgh/c^2 where P denotes the Peltier coefficient.

The work done against gravity in transmitting 10,000 kilowatts up 10,000 meters is about 100 ergs per second.

THE RICE INSTITUTE,
HOUSTON, TEXAS,
February, 1920.

QUANTUM EMISSION PHENOMENA IN RADIATION.

BY DAVID L. WEBSTER.

SYNOPSIS.

Comparison of X-rays and Light; a Summary.—This covers the best known cases of excitation of line spectra by electron impact, and *the form of the Bohr theory*, that is required by them.

Comparison of Emission and Absorption.—The above phenomena are compared with corresponding absorption phenomena, with especial reference to the accumulation of energy for photoelectrons by absorption.

Deductions.—Theories of the type of *Bohr's* appears *inconsistent with these facts.* The phenomena suggest that the law of the *conservation of energy*, as applied to atomic oscillators, *holds only statistically. A set of postulates to replace it* for individual oscillators is outlined.

COMPARISON OF X-RAYS AND LIGHT.

THE purpose of this paper is to compare the quantum phenomena in X-rays and light and to draw conclusions from them on the laws governing the emitting mechanism. Let us consider first the simpler

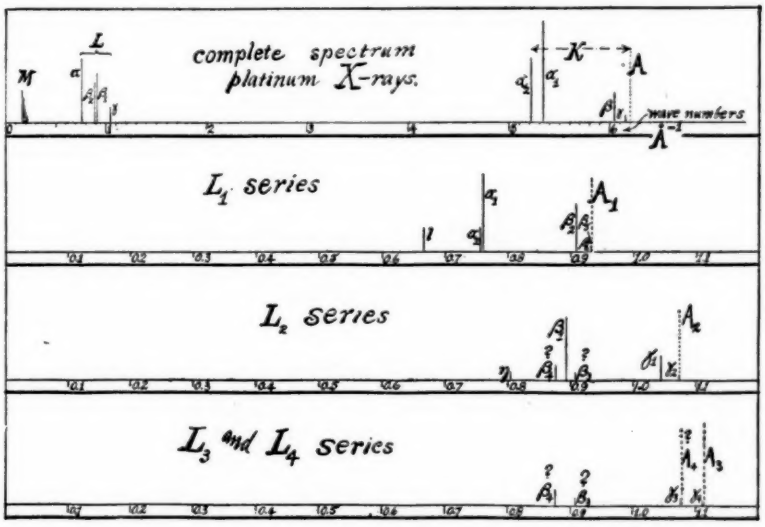

Fig. 1.

case of X-rays. In Fig. 1, we have the spectrum of platinum, on a scale of wave numbers, showing the K, L and M series. In the K series we

have the strong α lines, the weaker β and γ lines and the absorption limit A. This point A is especially important, because waves of a higher frequency than A are absorbed by the element much more strongly than those of lower frequency, and also the higher frequency waves give rise to a fluorescence consisting of the K series emission lines. If now we subject a piece of platinum to cathode rays, we should find no K series emission from it unless the energy of a single cathode ray is as large as a quantum of the frequency A. (This has not been tested directly for platinum, but has been for other elements,[1] and we may be sure they all act the same.) For any higher value of the cathode ray energy, we

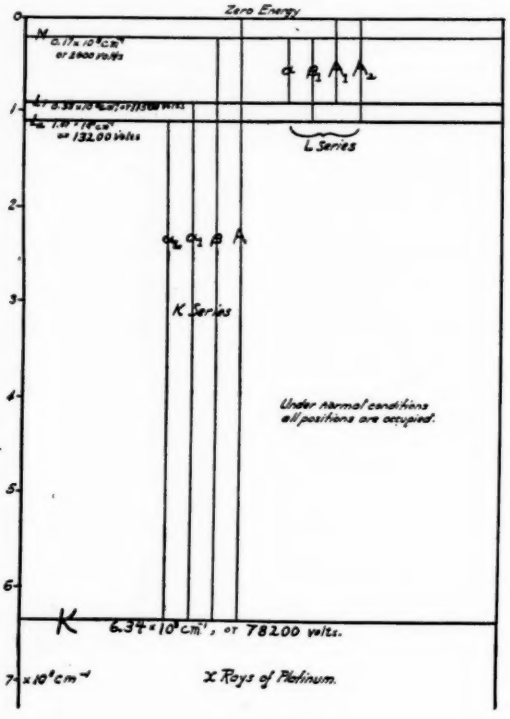

Fig. 2a.

have all the K series lines emitted with constant intensity ratios under all conditions. Evidently the mechanism used in the production of K series rays by cathode rays is such as to demand the same energy quantum as that used in fluorescence, and presumably it is the same mechanism.[2]

In the L series we have a similar state of affairs, except that the series must be divided into three or four sub-series, each with its own absorption

[1] For rhodium see D. L. Webster, PHYS. REV., 7, 599–613, June, 1916. For molybdenum and palladium see B. A. Wooten, PHYS. REV., 13, 71–86, Jan., 1919.

[2] D. L. Webster, l.c.

limit and corresponding critical potential. The exact status of the series marked L_3 and L_4 in the diagram is not settled, but L_1 and L_2 are definitely known to behave exactly like the K series as shown by evidence described elsewhere.[1] In every case the energy required is represented by many thousands of volts.

In light, however, conditions are different. For example, in sodium vapor, studied by Tate and Foote,[2] if the energy of the bombarding electrons is gradually increased there is no radiation till we reach 2.1

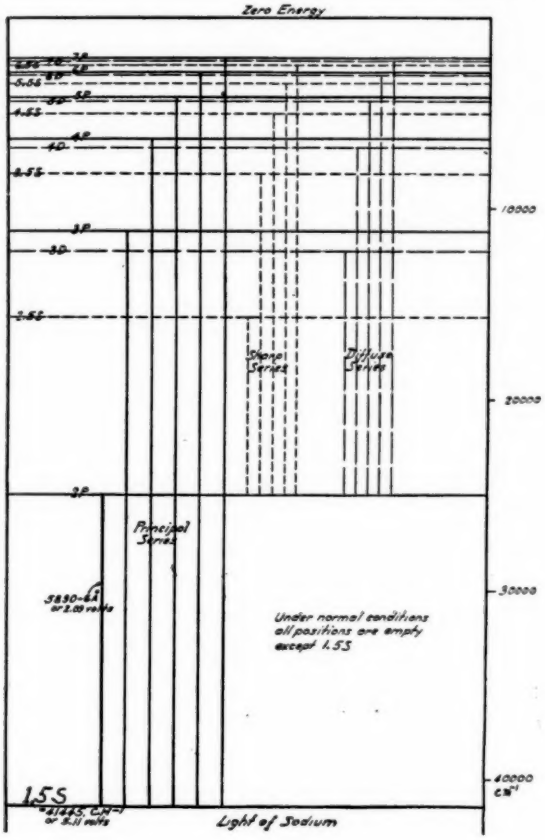

Fig. 2*b*.

volts, when the well-known D lines appear, alone, as a so-called "single-line spectrum." Now 2.1 volts corresponds exactly to the quantum of their frequency. But they are the first lines of a series, like the K α lines; and the limit of the series, corresponding to the point A, is at a

[1] D. L. Webster and H. Clark, Proc. Nat. Acad., *3*, 181–5, March, 1917, and D. L. Webster, ibid., Jan., 1920.

[2] J. T. Tate and P. D. Foote, Phil. Mag., *36*, 64–75, July, 1918.

frequency more than twice as high. The D lines are the lines $1.5S$–$2P$, and the limit, $1.5S$, corresponds to a voltage of 5.1 volts. When this voltage is reached, we get the whole series $1.5S$–mP, and with it the subordinate series, some of whose lines have lower frequencies than the D lines. The important difference from the X-ray case is the existence of the so-called "single-line spectrum," at voltages between 2.1 and 5.1 volts. Such a phenomenon is unknown in X-rays.

Now this difference between the two cases is readily explained by the diagram in Fig. 2. According to Kossel's[1] modification of the Bohr theory, the K series is produced by removing an electron from the innermost ring, called the K ring, and allowing one to fall into its place from another ring, the L, M or N. While I think there is ample evidence against the idea that the Bohr rings actually exist, it may be that the stable positions that do exist will act in much the same way. I have therefore drawn the diagram giving the K position at the bottom, indicating that a potential of 78,200 volts is required to lift the electron from it to the surface of the atom, where its energy would be zero. The energy required to do this is the quantum of the absorption limit, A, of the K series. Similarly the energies required to lift an electron from the L_1 and L_2 positions are the quanta of the absorption limits A_1 and A_2 respectively; and the K α lines are produced by removing an electron from the K position to infinity and replacing it by one falling from L_1 or L_2. By such considerations Bohr[2] predicted the fact that the critical potential for emission of the K series would be that which gives an electron a quantum of the frequency A, and Kossel, in 1914, predicted the relation $\nu_{K\alpha} = \nu_{KA} - \nu_{LA}$ which he tested as accurately as he could, and he also predicted some relations between emission line frequencies. An essential point for this explanation of the critical potential by Bohr and Kossel is that the electron removed from the K position *must* go to infinity, and cannot be allowed to come to rest in the L or M positions. That is, *in the normal atom all positions involved in X-ray processes are full.*

In light, on the other hand, we have a set of stable positions, shown in Fig. 2 as $1.5S$, $2P$, $2.5S$, $3P$, $3D$, etc., and the process of exciting the single line spectrum is evidently to lift an electron from $1.5S$ to $2P$ and let it fall back. If the electron is lifted to infinity, or zero energy, we shall excite the whole system, including the subordinate series. As van der Bijl[3] has suggested, the existence of the "single-line spectrum" means simply that *in the normal atom no position is filled above $1.5S$.*

[1] W. Kossel, Verh. d. D. Phys. Ges., Nov. 30, 1914.

[2] N. Bohr, Phil. Mag., *26*, 1–25, July, 1913.

[3] H. J. van der Bijl, PHYS. REV., *10*, 546–556, Nov., 1917. Van der Bijl does not call it the $1.5S$ ring, but describes it in terms equivalent to that.

In mercury, which has been studied by Frank and Hertz, McLennan and Henderson, Davis and Goucher and others, we have a more complex state of affairs indicated in Fig. 3. The lines $1.5S$–$2p_2$ and $1.5S$–$2P$ both appear at the potentials given by the quantum law, applied to their

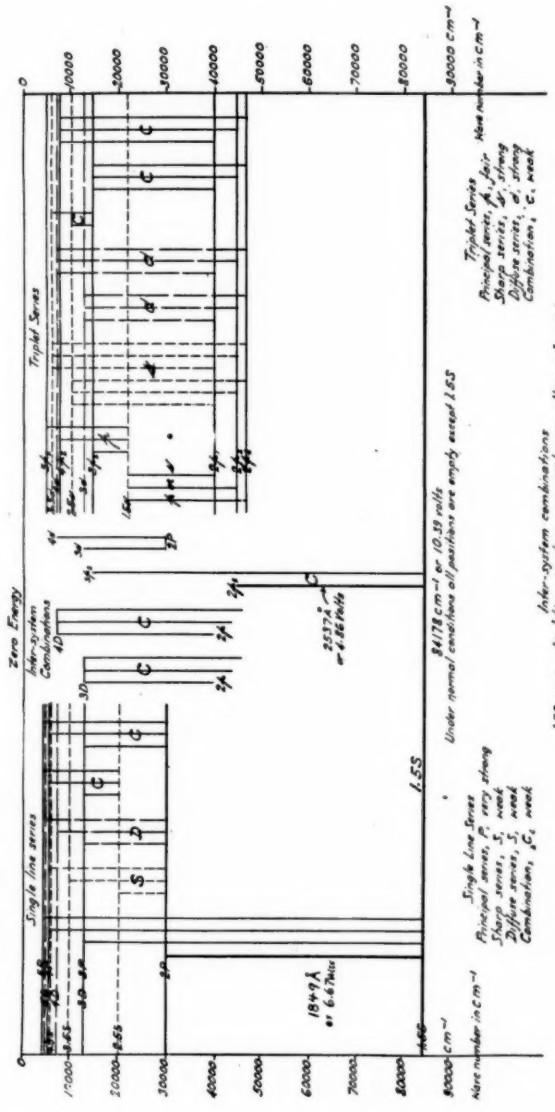
Zero Energy
Triplet Series
Inter-system Combinations
Single line series
1.5S
84178 cm⁻¹ or 10.39 volts
Under normal conditions all positions are empty except 1.5S
2537 Å = 4.86 Volts
1849 Å = 6.67 Volts
Triplet Series
Principal series, $^3P_1$, fair
Sharp series, $^3S_1$, strong
Diffuse series, $^3D_2$, strong
Combination, $^3C_1$, weak
Inter-system combinations
1.5S – mp_2; first line very strong, second known, others unknown;
2P – md_1; $2p_2$ – mD_2 fair
2P – ms_1; $3s_1$ – mP_1 weak
Single Line Series
Principal series, $^1P_1$ very strong
Sharp series, $^1S_0$ weak
Diffuse series, $^1D_2$ weak
Combination, $^1C_1$ weak
Wave number in cm⁻¹
cm⁻¹

Fig. 3.

respective frequencies, and the whole spectrum appears at the potential given by the quantum of $1.5S$. Again the explanation is van der Bijl's hypothesis that $1.5S$ is the only position that is normally full. In calcium also, effects exactly like those in mercury have recently been

observed by Mohler, Foote and Stimson,[1] and the explanation is again van der Bijl's hypothesis. These phenomena in light show clearly the existence of empty positions of stability, and if such empty positions were present in the X-ray mechanism they ought to show in the same way, by a "single-line spectrum" in each X-ray series. The fact that such a single line spectrum fails to occur is therefore strong evidence against any theory of X-rays that assumes empty positions of stability in the normal atom below the $1.5S$ position, as several of the recent theories do.

Comparison of Emission and Absorption.

So far the theory is good, and these elements are typical of the groups whose quantum emission phenomena are best known. When we apply the theory to absorption, referring again to Fig. 2, we see to some extent why it is possible to have sodium vapor absorb the D lines, and lift its electron to $2P$, and why it is impossible for any element to show selective absorption for any of its X-ray emission lines. Instead, it must absorb rays above the frequency A, since a quantum of such a frequency is required to remove the electron to a place where it can stay. But then the question arises, why can not the same process occur in light, and why does not sodium vapor absorb not only the D lines but also all frequencies above $1.5S$, and give a fluorescent spectrum under such conditions similar to X-ray fluorescence? Applied to absorption, this type of theory is most unsatisfactory.

A more fundamental difficulty appears when we consider the nature of the absorption process. The electron must in some way collect energy enough from the X-rays to appear as a photoelectron. This, according to Barkla,[2] means the amount $h(\nu + \nu_A)$, where ν is the frequency of the rays absorbed and ν_A is that of the absorption limit. This conclusion is drawn from the observed fractions of the total X-ray energy that appear in photoelectrons and in fluorescent X-rays and the fact that the photoelectrons all appear to have the same energy, $h\nu$. While the evidence on this latter point does not seem quite conclusive, it is significant that the energy $h(\nu + \nu_A)$ is exactly the amount suggested by the Bohr theory, although Barkla's evidence was not drawn at all from this theory. I say "suggested," rather than "required," because it is not certain that the electron could not be helped out of the atom by another electron falling in from an outer stable position as the first one goes out, thus neutralizing the force that would otherwise restrain the one that leaves.

[1] F. L. Mohler, P. D. Foote and H. F. Stimson, Bull. Bur. Stan., 1920. Abstract in PHYS. REV., *14*, 534, Dec., 1919.

[2] C. G. Barkla, Proc. Roy. Soc., A.*92*, 501–4, Aug., 1916.

However that may be, the electron leaves with energy of the order of $h\nu$ and must collect from somewhere a quantity of this order or perhaps $h(\nu + \nu_A)$. Millikan[1] has recently described experiments leading to conclusions of the same general type for photoelectrons produced by light.

Now where does the electron get this energy? If in light or X-rays the energy is all concentrated in a point of the wave front, the electron might get at once as much as the energy $h\nu$ of the primary cathode ray, but no more. But energy is the ability to do work; and to produce coördinated motions of electrons in different parts of a crystal, a train of waves of X-rays must have this ability at points widely scattered over the wave front and perpendicular to it. And in a reflected or scattered train of waves the whole energy is very much less than the quantum emitted from the primary radiator, according to any reasonable theory of these phenomena, so that the amount of energy coming within reach of any one atom exposed to this beam must be correspondingly reduced. In light, as shown by the diffraction pattern at the focus of a high-power microscope objective, the ability to do work must be distributed over practically a whole hemisphere of the wave front if not more, thus indicating a distribution of energy in light even wider than any we have definite evidence of in X-rays. It would be most unreasonable to assume that X-ray waves are not constructed like those of light, and probably the energy is distributed as widely in one case as in the other. If now the X-rays have passed through a slit, the wave train thus limited contains but a small fraction of a quantum, and if they are then reflected from a crystal it contains even less. The same is true of light subjected to such treatment. But in either case the photoelectron has as much energy when produced by the weakest beam as when produced by the strongest. And in X-rays photoelectrons can be obtained easily, as shown by ionization methods, when the heads of the successive wave trains are as far apart, on the average, as many millions of wave-lengths. One might perhaps attempt to explain the accumulation of energy by the coincidence of a large number of wave trains. But it is well known that this would not lead to a photoelectric current proportional to the intensity of the rays; and so it is evident that the absorption of energy by the photoelectron is not dependent upon coincidence. If not, then it must be by a process of gradual accumulation. According to the electromagnetic theory it would be very gradual indeed and, even in a strong monochromatic beam a resonating electron should take many weeks to acquire the energy $h\nu$. But aside from such theoretical considerations, the practical reasons given here seem sufficient to show the gradual nature of the process.

[1] R. A. Millikan, Am. Phys. Soc. meeting, Dec. 31, 1919.

Now let us suppose an electron from the K ring is absorbing X-rays and has lifted itself half way to the position of zero energy, and then is struck by a cathode ray. One would expect that if the cathode ray has only energy enough to lift the electron the rest of the way to the surface, it will produce the K series lines. But no. It must have a whole quantum of the critical frequency and no less. The same difficulty appears also in light, as one may see by reference to the phenomena described above.

In such a theory as I have just described there seems to be no way to distinguish the energy stored by absorption from the energy acquired from a cathode ray, and prevent them from being combined as suggested above. In a theory of heat radiation that I proposed in 1915,[1] based on Parson's magneton theory, the distinction might be made, because the energy accumulated by absorption was stored in a rotary form not readily affected by the impact of a cathode ray. But even here, there is some difficulty. The X-ray absorption spectrum is continuous, and it is hard to see how we can avoid the assumption that the natural absorption frequency of an electron is different at different times. Certainly it is not fixed by Bohr's energy considerations, because a larger quantum than $h\nu_A$ could not be collected continuously: the electron would escape as soon as it has the energy $h\nu_A$. Some other determining factor must be present. In light also, in solids and liquids, especially metals with free electrons, there must be continual changes and readjustments of the electron's frequency.

If now such a change of frequency occurs when an electron has nearly finished collecting a quantum, and the change is to a lower frequency, for which the energy already stored is more than a quantum, one would expect photoelectric action even if no rays happen to be falling on the electron when the change occurs. In this or some such way, one would expect some evidence of the stored energy to appear. Thus the magneton hypothesis, while distinctly better than the other, is still unsatisfactory, because evidence of stored energy fails to appear. The stored energy causes trouble, and perhaps more trouble than it is worth.

After all, what is it worth? As Poincaré[2] has said, every time we deal with a new type of phenomenon, we find or invent a new quantity that we can call energy, and define it so as to make the total energy of the system a constant. As both he and Ritz[3] have said, the law of the conservation of energy is not a law, but a postulate. Some time, a phe-

[1] D. L. Webster, Proc. Amer. Acad., *50*, 131–145, Jan., 1915; see also PHYS. REV., *8*, 66–9, July, 1916.

[2] H. Poincaré, Science and Hypothesis, Paris, 1901, Chapter VIII.

[3] W. Ritz, Ann. Chim. Phys., XIII, 145–275, or Collected Works, Paris, 1911, p. 345.

nomenon may arise where this postulate is not advantageous in its most complete form. It seems to me that this time has come. Explanations of phenomena are important, but a postulate is not.

To preserve our explanations of refraction and other classical phenomena of physical optics, let us assume as usual that the oscillator is governed by an equation of the form

$$m\ddot{x} + g\dot{x} + fx = eE_x,$$

x being the displacement of the electron from its equilibrium position and E_x the external electric force in the x direction. As Ritz suggested, a vibration controlled by a magnetic field or some similar agency is more probable than the elastic force fx, but as this is the usual form of dispersion equation, we may use it here. Any magnetic or similar vibration could be substituted without changing our present conclusions. This equation gives absorption at a rate $g\dot{x}^2$, the mean value of which through a whole period is $\frac{g}{m} U$ where U is the energy of the oscillation. Now, instead of assuming this absorbed energy to be stored somewhere, and reëmitted some time later, *let us assume it to be simply annihilated.* Then let us assume that the electron may at any time start an emitting oscillation of large amplitude, continuing uniformly until a whole quantum is radiated, or else emit a photoelectron with a quantum of energy. And let us assume that the probability of starting such an oscillation or photoelectron during a time dt is

$$\frac{g}{m} \frac{U}{Q} dt,$$

where Q is the "accumulated energy" defined above, which may be $h\nu$ or may be something larger. Further let us assume that transfers of energy either to or from cathode rays or other colliding particles can take place, but by quanta only.

That these hypotheses give a mathematical theory of dispersion exactly like the classical theory is evident from the fact that the dispersion theory is not concerned with what becomes of the power $g\dot{x}^2$ after it is taken from the electron by the damping force.

To make them give a theory of heat radiation we need only an entropy condition for the oscillator. To get this we may use almost the same condition as in my heat radiation theory, referred to above, which was modelled to a great extent on Planck's. If $Q = h\nu$, the behavior of an oscillator in a given field of radiation is almost equivalent to what is assumed there, because the rate of absorption and mean rate of emission

are the same. To make them exactly equivalent, we have only to assume that an oscillator newly formed in an atomic readjustment will behave almost exactly like the one of the other theory, which absorbed energy continuously and stored it, radiating by quanta or multiples of quanta. The only difference is that in starting its career with its new frequency it must not start at the zero of the scale of absorbed energy, but at any point on it, the probability of starting at any one point being proportional to the density of oscillators on the scale of energy at that point; and when it changes frequency again it must not be considered to have a store of energy in it. In other words, the stored energy of the previous theory must have been merely a mathematical fiction and should not have been assumed to have any real physical existence.

If the energy Q is greater than $h\nu$ we have a case of fluorescence, the energy $h\nu$ appearing in a photoelectron and the rest as fluorescent rays. In this case we get into the question of the thermodynamics of fluorescent bodies, which needs a long discussion. In the absence of very definite evidence on the exact value of Q, as suggested above, the time does not seem ripe for such a theory.

SUMMARY.

We may summarize these conclusions as follows: The simple Bohr theory is good for explaining the phenomena of excitation of X-rays and light by impact, if we assume that in the normal atom all rings are full from the K ring to the $1.5S$ ring, inclusive, but none outside $1.5S$. But the theory is quite unsatisfactory for absorption phenomena. Even if the absorbing electron is not a member of a Bohr ring, but a "magneton" of the type assumed in my previous theory, situated in a stable position similar to a Bohr ring, and having the required resonance frequency, there are still some difficulties when the frequency is subject to change with time. Consequently it seems better to assume that in postulating the existence of stored energy in the oscillator we have carried the postulate of conservation of energy a step too far. We had better abandon it at this point and postulate a system of equations that give the conservation of energy as a statistical effect only and preserve the explanations of dispersion and heat radiation intact, at the same time explaining the phenomena of excitation of radiation by impact.

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IONIZATION POTENTIALS OF ARGON, NITROGEN, CARBON MONOXIDE, HELIUM, HYDROGEN AND MERCURY AND IODINE VAPORS.

BY CLIFTON G. FOUND.

SYNOPSIS.

Measurement of the Ionization potential of Gases was accomplished by means of a two electrode tube, by determining the point on the current-voltage curve at which the current increases at a rate faster than that given by Langmuir's equation

$$i = A(V + V_0)^{3/2}.$$

The effect of a voltage drop along the cathode was eliminated by a commutator arrangement which broke the filament heating circuit while the electron current was being measured.

The initial velocity of the electrons, V_0, was determined directly from the current-voltage curve.

Ionization potentials were obtained by measurement as follows: Argon 15.6, nitrogen 15.8, carbon monoxide 15.0, hydrogen 15.1, helium 20.5, mercury vapor 10.1, iodine vapor 8.5. The ionization potential of *argon* was found to be constant for pressures between 1 and 200 bars.

INTRODUCTION.

IT has been shown by Langmuir[1] that for a pure electron discharge, when the electrons start from the cathode with zero velocity, the maximum current which will pass to the anode is given by

$$i = A V^{3/2}, \qquad (1)$$

where V is the voltage on the anode and A is a constant, depending only on the geometry of the tube.

The limitation of current is caused by space charge or the negative electrostatic field due to the electrons in the space between the electrodes. If in any way the effect of this negative space charge is neutralized, the current to the anode will increase with the voltage faster than the rate given by equation 1. One way of neutralizing space charge is by the presence of positive ions. Hence, if an electron tube contains gas, as soon as positive ions are produced, the current increases more rapidly with increase of voltage, causing a point of discontinuity in the volt-ampere characteristic curve.

The voltage at which this kink occurs is a measure of the ionization potential of the contained gas.

[1] PHYSICAL REVIEW, Vol. 11, No. 6, Dec., 1913.

In the above reasoning, it was assumed that the electrons started with zero velocity, but in practice they are emitted with an initial velocity. If the average initial velocity is equal to a voltage *Vo*, then equation (1) becomes

$$i = A(V + V_0)^{3/2}. \qquad (2)$$

Thus a voltage must be added to the observed voltage at which the kink occurs in order to obtain the true ionization potential. Tate and Foote,[1] Foote and Mohler[2] and others have determined the ionization potentials of a number of metallic vapors from the position of the kink in the volt-ampere characteristic curve. The value of V_0 they determined from measurements of resonance potentials.

The present method differs from that of Tate and Foote in that the ionization potential in this case is determined directly from equation (2) which does not hold rigorously for their arrangement. The facts that there was a difference of potential between the end of the cathode due to the heating current and also that a third electrode at a voltage negative to the anode was present, would prevent the current increasing, at low voltages, at a rate as high as that given by equation (2).

In order to eliminate the effect of a voltage drop along the filament, the present measurements were made with a rotating commutator. The diagram of connections is shown in Fig. 1. The rotating commutator is

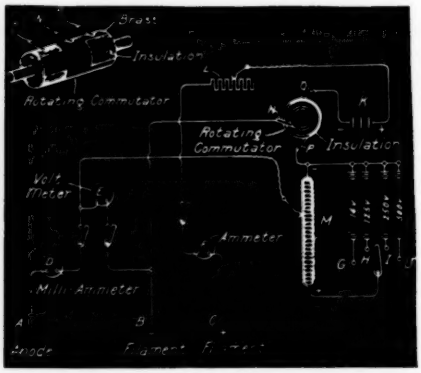

Fig. 1.

Diagram of electric connections for measuring the volt-ampere characteristics of vacuum tubes by use of rotating commutator.

so connected that no current can flow to the anode while the heating current is passing through the filament and the anode current is measured during the interval the heating circuit is broken. The speed of the com-

[1] Phil. Mag., *36*, 1918.

[2] Phil. Mag., *37*, Jan., 1919.

mutator is so great that there is no appreciable cooling of the filament during the intervals in which the heating current is off. The voltage of the anode and the anode current were measured on direct current instruments. Since these were on only a portion of the time, the readings obtained were average values and in order to obtain effective values, it is necessary to multiply the observed values by a constant—corresponding to the reciprocal of the fraction of the time during which current flowed. This constant was determined by taking the ratio of the voltage with commutator stopped, to the voltage reading with commutator running.

In all cases, the values given in the tables are effective values, obtained from the observed values by multiplying by the commutator constant. This varied from 2.18 to 2.22. The variation was due to resetting of the commutator brushes and in no case was a variation found during any series of measurements.

The electron tube which was used for these measurements consisted of two tungsten filaments, each wound in the form of a double helix, and molybdenum cylinder about 12 mm. diameter and 12 mm. long. The helices and cylinder were arranged coaxially. The inner helix, which was 5 turns of 0.125 mm. wire wound on a 2.25 mm. mandrel, was used as cathode. The outer helix, which had 3 turns of 0.125 mm. wire wound on 3.65 mm. mandrel, was connected to the molybdenum, cylinder and the combination was made the anode. This arrangement has the advantage that the electrons travel from the outer helix to the cylinder with a uniform velocity equivalent to the anode voltage so that when ionization takes place a larger number of positive ions is formed than if the outer helix were not present.

Since most of the positive ions travel to the cathode, a larger number is present in the region between the helices than would be present if the electrons did not travel over a large portion of their path with the maximum velocity corresponding to the anode voltage.

Calculation of Ionization Potential.

To determine the ionization potential of a gas, the volt-ampere characteristic of the tube was first taken with a good vacuum (about .001 bars), while it was still connected to a Langmuir condensation pump. The tube was then shut off from the pump by means of a mercury trap separated from the former by a liquid air trap and a known pressure of the gas let in. The characteristics were then taken again with the gas present.

The value of V_0 was calculated from equation (2). If i_1 and i_2 are the electron currents at two voltages V_1 and V_2 respectively, below the

ionization potential, when gas was present, then

$$\frac{i_1}{i_2} = \left\{ \frac{V_1 + V_0}{V_2 + V_0} \right\}^{3/2}$$

or

$$V_0 = \frac{V_1 - \left\{ \frac{i_1}{i_2} \right\}^{2/3} V_2}{\left\{ \frac{i_1}{i_2} \right\}^{2/3} - 1}. \tag{3}$$

If $V_2 = 0$

$$V_0 = \frac{V_1}{\left\{ \frac{i_1)}{i_2)} \right\}^{2/3} - 1}. \tag{4}$$

The value of V_0 was calculated from (3) and (4) for a number of observations and the average value taken. The values of V_0 for any characteristic curve did not differ by more than .2 volts.

It was found that the constant A decreased when a relatively large pressure of gas was present. This can be accounted for by the increased distance the electrons have to travel in reaching the anode, due to collisions with the gas molecules. It is equivalent to an increase in the distance between electrodes. It was found, however, that the relation

$$i = A(V + V_0)^{3/2}$$

held up to the highest pressures at which measurements were taken. This was about 1,000 bars for argon, helium, carbon monoxide and nitrogen, while for hydrogen and mercury and iodine vapors, the highest pressures were those given in the tables below. This is in agreement with the results of Richardson and Bazzoni,[1] who found that the three halves power law held at low voltages in mercury vapor up to about 1 mm. pressure. In order to bring the characteristics when gas was present to correspond to those with a good vacuum, at voltages below ionization, it was found necessary to multiply the electron currents with gas by a constant K. The value of K was determined by comparing values of i at corresponding voltages below the ionization potential.

EXPERIMENTAL RESULTS.

Table I. gives the tabulated results for argon, at a number of pressures. The values of P, V_0 and K calculated as described above are given in the horizontal columns while vertically beneath them are given the values of Ki which are the observed values of the current multiplied by the factor K in order that the results with different pressures may be comparable.

[1] Phil. Mag., 32, 1916, p. 426.

TABLE I.

Argon.

P (Bars).....	.001	1	6.1	35	80	280
V_0 (Volts)....	.95	1.0	1.0	1.0	.95	.95
K.....	1.00	1.00	1.00	1.00	1.06	1.20
$(V+V_0)^{3/2}$	Ki	Ki	Ki	Ki	Ki	Ki
5.7	.41	.41	.43	.38	.38	.39
12.2	.95	.89	.92	.90	.90	.90
20.0	1.55	1.56	1.50	1.54	1.51	1.55
24.8	1.85	1.85	1.84	1.85	1.85	1.83
35.0	2.56	2.55	2.54	2.57	2.57	2.58
46	3.36	3.31	3.32	3.35	3.30	3.25
52	3.78	3.75	3.74	3.80	3.85	3.75
58	4.22	4.20	4.19	4.22	4.22	4.23
62	4.50	4.65	4.65	4.49	4.42	4.50
64	4.75	4.85	4.81	4.85	4.60	4.80
69	5.00	5.09	5.09	5.20	5.15	5.40
71.5	5.28	5.28	5.28	5.53	6.10	6.85
78	5.80	5.90	6.15	7.0	8.25	13.4
86	6.20	6.55	6.55	8.9	13.1	——
92	6.90	7.00	7.70	11.6	20.6	——
100	7.20	7.65	8.80	15.5	——	——

Ionization potential = $(62)^{2/3}$ or 15.6 volts.

TABLE II.

Argon.

P (Bars).....	1	6.1	35	80	280
$(V+V_0)^{3/2}$	Δi	Δi	Δi	Δi	Δi
5.7	.00	.02	−.03	−.03	−.02
12.2	−.06	−.03	−.05	−.05	−.05
20.0	.01	−.05	−.01	−.04	.00
24.8	.00	−.01	−.00	.00	−.02
35.0	−.01	−.02	+.01	+.01	+.02
46.0	−.05	−.04	−.01	−.06	−.11
52.0	.03	−.04	.02	.07	−.03
58.0	−.02	−.03	.00	.00	+.01
62.0	.15	.15	−.01	−.08	.00
64	.10	.06	.10	−.15	.05
69	.09	.09	.20	.15	.40
71.5	.00	.00	.25	.82	1.57
78	.10	.35	1.20	2.45	7.60
86	.35	.35	2.7	6.9	——
92	.1	.80	4.7	13.7	——
100	.45	1.60	8.3	——	——

Ionization potential = $(62)^{2/3}$ or 15.6 volts.

The first vertical column gives the effective values of anode voltage raised to the three-halves power. Table II. gives the difference between the electron current in a good vacuum and that when gas is present.

Figure 2 gives the plot between the electron current and the effective

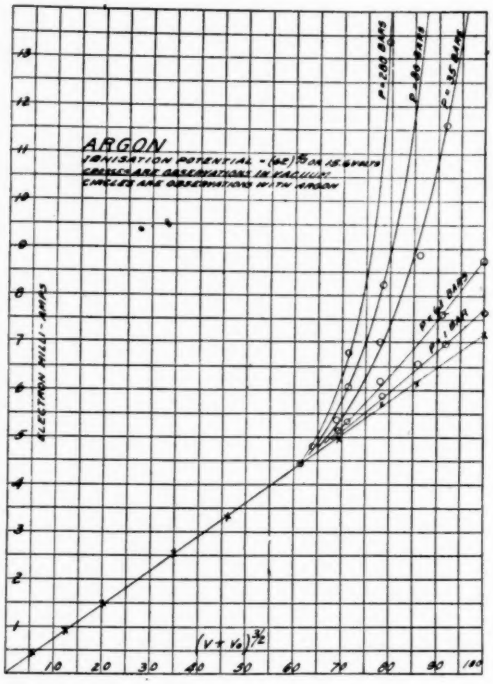

Fig. 2.

voltage raised to the three-halves power. It will be noted that the curve for a good vacuum is linear throughout the entire range while the curves when gas is present are linear only up to a certain point, above which the current increases faster than the linear relation. The curves for pressures from 1 to 280 bars apparently begin to depart from a straight line at the same point and the rate of departure increases with the pressure. At the lower pressures, it is difficult to tell the exact point at which the departure commences, but at the higher pressures the curve when gas is present meets that for a good vacuum at a sharp angle and there is no doubt where the effect of ionization sets in. For this reason, a high pressure of gas was used to determine the ionization potentials of the other gases.

Table III. contains the results for nitrogen. The first column gives the three-halves power of the effective voltage. The second and third

give the corresponding values of the electron current with gas present and in a good vacuum, while the last column gives the difference between columns two and three. Figure 3 shows plot of results with nitrogen.

TABLE III.

Nitrogen.

P (Bars).....	300	.001	
V_0 (Volts).....	1.6	1.1	
K.....	1.14	1.00	
$(V+V_0)^{3/2}$	Ki	i	Δi
4.45	.35	−.31	.04
10.9	.76	.74	.02
18.8	1.36	1.29	.07
28.0	1.96	1.92	.04
38.6	2.65	2.68	−.03
50.5	3.40	3.43	−.03
53	3.60	3.64	−.04
56	4.00	3.84	.16
59.5	4.20	4.08	.12
63	4.45	4.32	.13
66	5.10	4.52	.58
69	6.50	4.74	1.76
73	8.40	5.00	3.40
76	11.6	5.20	6.40

Ionization potential = $(63)^{2/3}$ or 15.8 volts.

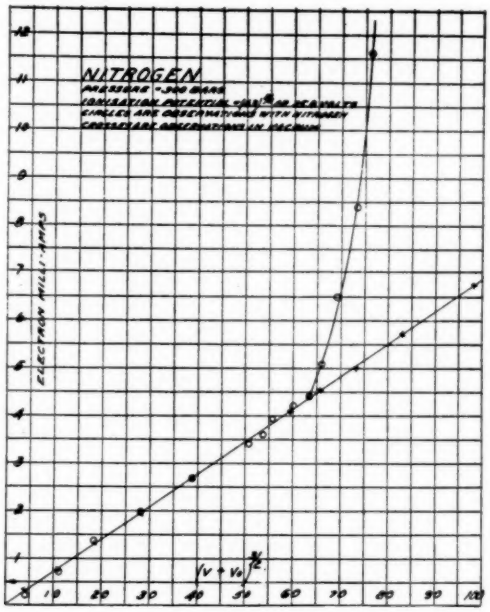

Fig. 3.

Tables IV., V., VI., VII., VIII. give the results for carbon monoxide, hydrogen, helium, mercury vapor and iodine vapor respectively, while Figs. 4, 5, 6, 7 and 8 give the corresponding curves.

TABLE IV.

Carbon Monoxide.

P (Bars)..... V_0 (Volts)..... K.....	200 2.2 1.03	.001 1.1 1.00	
$(V+V_0)^{3/2}$	Ki	i	Δi
6.0	.51	.57	−.06
12.9	1.14	1.19	−.05
21.5	1.90	1.96	−.06
31	2.80	2.80	.00
42	3.65	3.68	−.03
51	4.55	4.55	.00
54	4.85	4.85	.00
58	5.10	5.10	.00
61	6.00	5.40	.60
64	8.20	5.55	2.65
67	12.00	5.82	6.18
74	20.6	6.60	14.0
81	32.0	7.38	24.6

Ionization potential = $(58)^{2/3}$ or 15. volts.

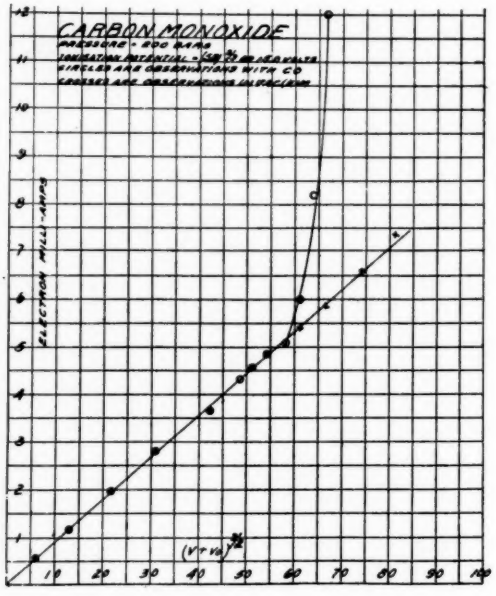

Fig. 4.

Table V.

Hydrogen.

P (Bars) ..... V_0 (Volts) ..... K	135 2.5 1.2	.001 1.1 1.00	
$(V+V_0)^{2/3}$	Ki	i	Δi
6.8	.38	.48	.10
13.7	1.00	.95	−.05
22.0	1.58	1.52	.06
31.5	2.23	2.18	.05
40	2.75	2.75	.00
48	3.35	3.32	.03
54	3.78	3.74	.04
57	4.01	3.96	.05
60	4.22	4.17	.05
63	4.45	4.38	.07
65	4.70	4.52	.18
68	5.10	4.72	.38
73	5.63	5.06	.57
86	8.00	5.92	2.08

Ionization potential = $(59)^{2/3}$ or 15.1 volts.

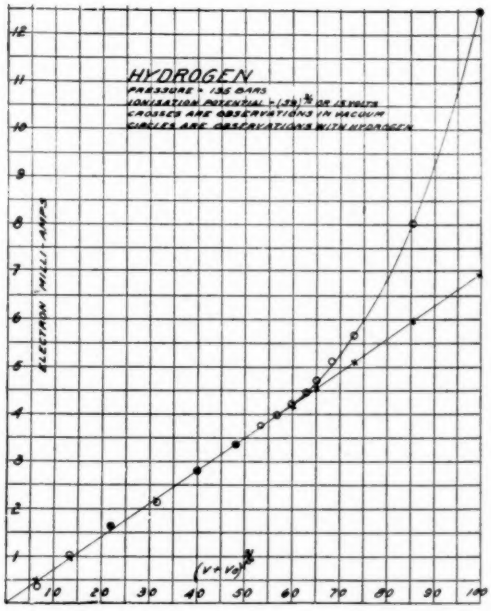

Fig. 5.

TABLE VI.

Helium.

P (Bars).....	650	Vacuum	
V_0 (Volts).....	2.3	2.2	
K.....	1.60	1.00	
$(V+V_0)^{3/2}$.....	Ki	i	Δi
6	.123	.176	−.53
13	.220	.275	−.55
21.5	.358	.385	−.27
31.1	.520	.530	−.10
42	.700	.700	.00
54	.91	.900	.10
67	1.12	1.12	.00
74	1.28	1.23	.05
81	1.47	1.36	.11
88	1.68	1.50	.18
96	1.95	1.60	.35
103	2.47	1.74	.73
112	3.10	1.85	1.25
120	3.68	1.96	1.72

Ionization potential = $(94)^{2/3}$ or 20.5.

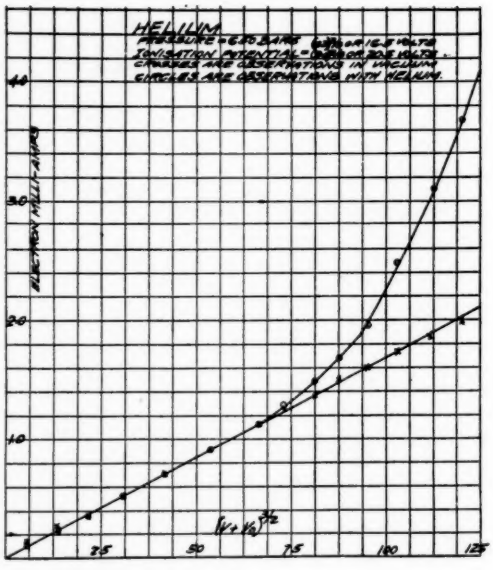

Fig. 6.

TABLE VII.

Mercury Vapor.

P (Bars)..... V_0 (Volts)..... K.....	2.0 2.75 2.0	.001 2.2 1.0	
$(V+V_0)^{3/2}$	Ki	i	Δi
4.6	.84	.84	.00
11.2	2.15	2.15	.00
15	2.75	2.85	−.10
19.4	3.63	3.74	−.11
24.0	4.45	4.55	−.10
26.5	5.20	5.20	.00
29	5.80	5.60	.20
32	6.20	6.10	.10
33	6.65	6.40	.25
34	7.20	6.50	.70
35	8.20	6.70	1.50
36	9.50	6.85	2.65
37	11.0	7.09	3.91

Ionization potential = $(32)^{2/3}$ or 10.1 volts.

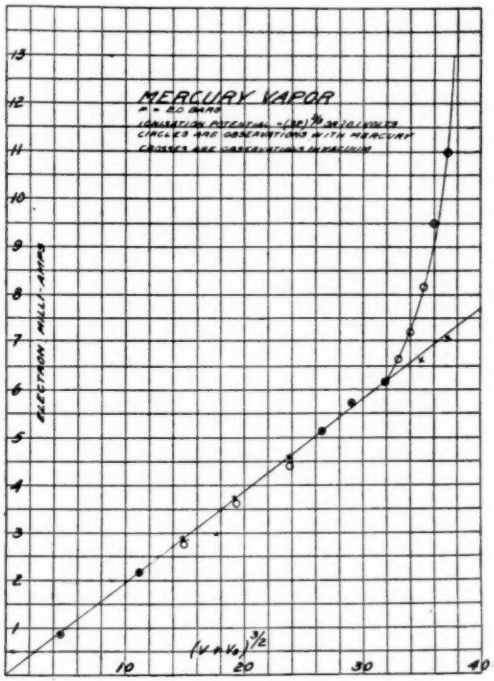

Fig. 7.

TABLE VIII.

Iodine Vapor.

P (Bars)	40	.001	
V_0 (Volts)	.35	1.6	
K	2.5	1.0	
$(V+V_0)^{2/3}$	Ki	i	Δi
4.3	.35	.32	.03
10.9	.78	.77	.01
19.4	1.44	1.45	−.01
24.2	1.80	1.80	.00
25.0	1.90	1.87	.03
26.1	2.00	1.95	.05
27.2	2.10	2.03	.07
28.2	2.30	2.10	.20
29.5	2.40	2.25	.15
30.5	2.54	2.32	.22
31.5	2.77	2.40	.37
32.6	3.25	2.48	.77
33.5	3.75	2.57	1.18
37.0	5.25	2.80	2.45

Ionization potential = $(25)^{2/3}$ or 8.5 volts.

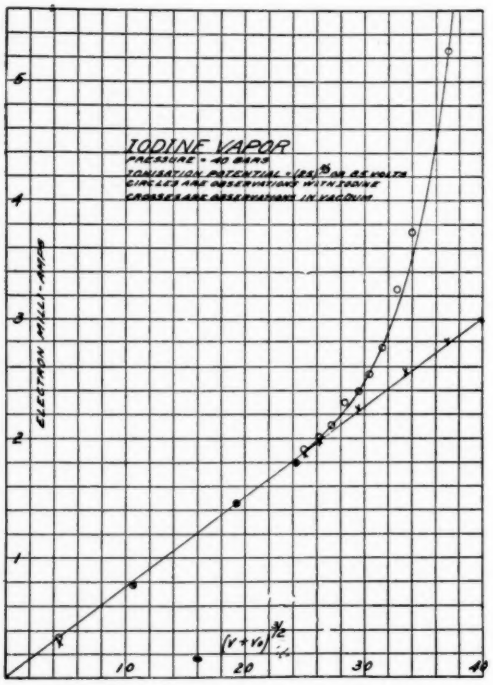

Fig. 8.

The curve for helium shows two kinks, the first one at 16.5 volts and the second at about 20 volts. One explanation that might be given for these results is that helium has two types of ionization, a weak one occurring at 16.5 volts and a more intense one at 20 volts. Since no other experimenter has found ionization in helium as low as 16.5 volts, it seems more probable that this value is due to a slight impurity in the helium, although the latter was purified by passing through charcoal at the temperature of liquid air. The helium used was known to contain a slight admixture of neon, which would not be removed, as it passed through the charcoal at the temperature of liquid air. Since it would require only about 6 bars or 1 per cent. of neon to account for the magnitude of the kink at 16.5 volts, it seems very probable that this kink is due to ionization of the neon content, while the ionization potential of helium is given by the second kink at 20.5 volts.

SUMMARY.

1. It has been shown that the relation

$$i = A(V + Vo)^{3/2}$$

holds for the electron tube used in these experiments when no gas is present.

2. When gas is present, the above relation holds up to a certain voltage corresponding to the ionization potential of the gas, beyond which the current increases at a faster rate than given by the equation.

3. From the location of the point of departure from the above relation, the ionization potentials given in Table IX. were determined.

TABLE IX.

Gas.	Ionization Potential.
Argon	15.6
Nitrogen	15.8
Carbon Monoxide	15.0
Hydrogen	15.1
Helium	20.5
Mercury vapor	10.1
Iodine vapor	8.5

In conclusion, the writer wishes to express his appreciation of the kindly interest taken in these experiments by Dr. Langmuir, whose suggestions proved most valuable.

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NEW FACTS ABOUT SURFACE-FRICTION.

BY CH. TERZAGHI.

SYNOPSIS.

Friction between Smooth Surfaces: Physical Properties of Clays.—In the present paper the author discusses a number of preliminary experiments leading to an investigation of the physical properties of clays. Since plastic deformations of clay-bodies involve the sliding of the smooth clay particles upon each other, in order to determine the character and the laws governing the frictional forces, the author studies the behavior of smooth glass plates placed in contact under different conditions of loading. As a result of these experiments it is established that the frictional resistance between two surfaces is not due to the shearing strength of a cushion of air or water; but to the existence of microscopic particles that deposit themselves on the rubbing surfaces. Frictional resistance was found to be independent of the thickness of the air cushion.

Properties of Very Thin Layers of Water; Permeability and Water Contents of Clays.—A drop of water was placed between two glass plates and was allowed to evaporate. When the thickness of the layer of water was reduced to about 100 $\mu\mu$, the evaporation stopped completely, suggesting that the molecules of a solid are able to exert forces over distances of the order of 50 $\mu\mu$. Such thin layers of water have, beside viscosity, shearing and tensile strength. The author uses this result to explain the facts: (1) that layers of clay are impermeable unless the head exceeds a certain minimum; (2) that the water contents of clays do not drop below a certain limit; (3) that a drop of water does not spread over a surface wetted by water.

Theory of Surface Friction.—As a result of the observations mentioned and of a new set of experiments, the author concludes that the ordinary laws of friction of rest apply only where contact between the rubbing surfaces must be enforced by outside pressure. When two even surfaces are in contact the explanation of the causes of friction is not so simple on account of the presence of small particles on the surfaces.

THE following article may be considered as a preliminary report on a series of investigations carried out by the author in the Laboratories of *Robert College*, Constantinople (Branch institution of *N. Y. State University*).

I. INTRODUCTION.

Most of the properties of clays, as well as the physical causes of those few properties that have been investigated, are unknown. We know nothing about the elasticity of clays, or the conditions that determine their water capacity, or the relations between their water content and their viscosity, or the earth pressure that they exert and not even about the physical causes of the swelling of wetted clays. As a consequence

the civil engineer, dealing with this important material, is at the mercy of some unreliable empirical rules, and laboratory work carried out with clays leads only to a mass of incoherent facts. In order to establish a reliable theoretical basis for his practical investigations, the author has endeavored to solve the following questions: Is it possible to explain the physical properties of clays by means of the ordinary laws of physics (surface friction as a force, proportional to the surface pressure, acting merely in tangential direction, the laws of capillarity and the law of Darcy) or are we obliged to modify these laws in their application to the physics of colloidal matter?

II. SURFACE FRICTION BETWEEN BODIES WITH SMOOTH SURFACES.

Microscopical examination of clays shows that clay consists of a loose mass of small, transparent bodies with more or less smooth surfaces. Every plastic deformation of a clay-body involves the sliding of such surfaces on each other. No process can better be compared with this phenomenon than the sliding of two glass-plates on each other. But the question arises, as to whether the sliding of glass-plates on each other takes place under the same physical conditions as the relative motion of two grains of clay, and if not, what is the essential difference between the two cases of friction? The dealing with this fundamental question has forced the author to a new conception of the physical causes of friction of rest. This conception is evolved as a natural consequence of the following experiments:

1. A glass-plate with an even surface was laid on the table and covered by another one of the same size and quality. The surface of contact showed next to one of the corners a green spot surrounded by Newton's rings, the rest of the surface remained colorless. By pressing the colored spot with a glass-stick the color of the center became a yellow of the first order, indicating a thickness of 140 $\mu\mu$ (0.00014 mm.) for the air cushion separating the two sheets, no further approach of the two glass plates being possible. The observation revealed the fact that the original green color of the center was of the fifth order corresponding to a distance of more than 1 μ (0.001 mm.) and that this distance represented the minimum distance between the two bodies in unloaded condition. The experiment has been very often repeated, but the coloration and the location of the colored spot was always different, the only fact in common to the observed phenomena was the fact, that the minimum distance between the two plates never dropped below 1 μ.

2. Two square glass-plates of 2 x 2 cm., 0.15 mm. thick, were provided with a system of fine scratches. The average width of these scratches

was 0.2 μ. By means of these scratches a map has been plotted of the air cushion separating the two sheets. The minimum distance between the sheets was found to be 3.7 μ, the maximum distance 32 μ. This experiment too was several times repeated, always with approximately the same result, but the spot of minimum distance changing its location.

3. Thirty four of the above-mentioned square glass-plates were placed one upon the other, so that they formed a prism of a total weight of 4.3 gr. This prism was placed under the microscope and gradually loaded up to a total load of 100 gr. The first application of the load resulted in a permanent settlement of 3 μ per glass-sheet. At each new application the permanent settlement became smaller and finally the prism assumed the character of a perfectly elastic body whose modulus of elasticity increased rapidly with the load. By increasing the load from 2.85 gr. to 23 gr. per cm.^{2}, the total average compression was measured to be 4.17 μ per sheet. The same experiment was repeated with the glass-sheets placed under water. The result of the loading test was practically the same, with the only difference, that an increase of the load from 2.85 to 23 gr. resulted in a compression of 4.85 μ per sheet. In both cases the application of additional load was immediately followed by deformation.

The following experiments were devoted to an endeavor to find out the nature of the force that prevents the glass-sheets from touching. If the two glass-sheets were separated by an air or water cushion only, experiment No. 2 would have shown that:

(*a*) The thickness of the cushion would decrease with increasing load.

(*b*) The frictional resistance between the two surfaces would be due to the shearing strength of the cushion; and as experience shows that frictional resistance increases in approximately direct proportion with the load we would have to conclude:

(*c*) That the shearing strength of a cushion of given area increases with decreasing thickness.

4. Two glass-prisms with particularly smooth surfaces were placed one above the other and the frictional resistance between the two bodies was directly measured by means of an accurate balance. After each experiment, the two surfaces were carefully rubbed with a cloth and freed from dust with a camel-hair brush. The distance between the two surfaces was indicated by the visible interference effect and varied between the very wide limits of 0.6 and more than 1.2 μ. Frictional resistance was found to be *independent* of the thickness of the air cushion.

5. The same prisms were placed 2 cm. below the surface of distilled

water. Increase of water pressure up to 30 cm. did not effect their mutual distance. The third and fourth experiment show that the thick air and water cushions observed in the first and second experiment cannot be considered as the seat of the forces that keep the surfaces apart. The spacing was afterwards found to be produced by bodies of microscopical size, enclosed between the two surfaces. It must be simply considered as a statistical law, similar to the laws that determine the death-rate and the number of suicides in cities, that, as soon as a surface is exposed to air or water, a certain number of small fragments attach themselves to it and the dimensions of the three biggest particles determine distance as well as frictional resistance. That must be considered as the cause why there does not exist any definite coefficient of friction between glass and glass. The angle of friction varies between the limits of 1° and 10° and the case of friction at moderate pressure between the smooth surfaces of two bodies which are *not* separated by a third, one cannot be realized except in microscopical dimensions.

6. A glass sheet of 2 x 2 cm., 0.15 mm. thick was fixed to the upper surface of a glass plate of bigger dimensions by means of a drop of water enclosed between the two bodies. The temperature in the room being 28° C. the water evaporated rapidly until several wet spots remained, surrounded by Newton's rings. The thickness of the water-cushion could be estimated to be about 100 $\mu\mu$. A great number of such couples were produced in a similar way and the result was always the same. Several water spots have been systematically examined under the microscope for enclosed microscopical bodies and typographical maps have been plotted indicating position and dimension of every obstacle. In every water spot a certain number of fine crystal-leaves could be located, but while in most of the spots the leaves were simply enclosed between the two surfaces, in one spot two particles have been discovered indicating by their coloration, that they stood under very high pressure. Simultaneous evaporation tests have been carried on. Water with its surface 2 cm. below the upper edge of a narrow glass-tube evaporated with a rate of about 1 mm. per day. A water surface 8 cm. below the top of a similar tube went down with a rate of about 0.3 mm. per day, while the water spots between the glass-sheets did not show any measurable sign of evaporation, even those which joined the outer edge of the glass-sheet, even although they have been purposely exposed for several days to the sun and to the wind.

The results of this experiment indicate clearly, that a water-cushion of less than 100 $\mu\mu$ has properties which are different from the properties of larger bodies of water. The low rate of evaporation can be explained

in two different ways; Either the surface of the edge of the waterspot is covered by a layer of saturated vapor that is kept from diffusion by molecular attraction through the molecules of the solid body, or the water-molecules are kept in their position by the same forces. But if the molecules of the solid body are able to act over a distance of more than 50 $\mu\mu$ on the rapidly travelling molecules of saturated vapor, the more they will exercise their solidifying influence on the quieter molecules of water within the same range of distance. The distance of 50 $\mu\mu$ is identical with the distance (measured by Quincke)[1] up to which glass is able to influence the angle of contact between water and silver.

Combining the result of experiment No. 6 with the fact (observed by Seelheim and discussed by Forchheimer)[2] that layers of clay are impermeable unless the head exceeds a certain minimum, which is a function of the thickness of the layer, we are now obliged to attribute to the surface layer both the qualities of a solid and of a liquid, at least in the case where such surfaces meet each other between the surfaces of two solid bodies. This involves within the film of the liquid not only viscosity but shearing- and tensile-strength too.

The double thickness 0.1 μ of the contact-layer is the approximate width of voids in a thickly packed mass of grains whose size is smaller than 1 or 2 μ. According to Atterberg[3] no powder with uniform size of grains shows plasticity unless its particles are smaller than 2 μ.

Experiment No. 6 explains the fact, observed by the author, that the water content of a clay exposed to the air at ordinary temperature does not drop below a certain limit ranging between 4 and 8 per cent. of the weight of the dry matter (the exact value depending on the size and particularly on the shape of the grains).

The fact that the influence of the molecules of the solid body is exerted up to a distance of more than 50 $\mu\mu$ from the surface seems to bear a relation with the unexplained fact, that a drop of water does not spread over a surface wetted by the water, but that its surface slopes down to the surface on which it rests, forming with it a certain angle of contact. If the influence of the molecules of the solid body were limited to a distance equal to the thickness of the surface layer of the liquid (0.06 $\mu\mu$), the mentioned effect would not be possible as a simple statical consideration shows. The author explains the phenomenon as follows: The surface layer of the waterdrop is not anchored to the surface AB of the glass-sheet (Fig. 1) but to the semi-solid surface layer $ABCD$ and is therefore unable to spread because the area of this layer is limited. Another

[1] Annales de Chimie et de Physique.

[2] Ztsch. d. Ver. d. Ing., 1901.

[3] International reports on pedology, 1913.

simple experiment made with an eye-glass and a wet handkerchief indicated too the semi-solid character of thin films of water. Sweeping the handkerchief over the glass, the glass surface was covered with a thin film of liquid showing interference-colors. The surface of drops of water placed upon this film formed with it an angle of contact just as

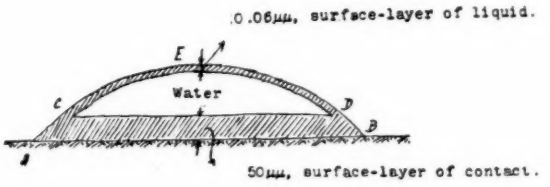

Fig. 1.

they would do it they were immediately placed on the glass surface, they showed no tendency to spread and their behavior was not at all influenced by the gradual evaporation of the film that surrounded them. While the film itself did not contract to drops as a thicker film would do but it retained its original relief until it evaporated.

III. Elastic Theory of Surface-Friction of Rest.

Under the influence of the results of his observations the author assumes that surface-friction stands in direct proportion to the area of those parts of their surfaces which are closer to each other than 0.1 μ (called area of contact) and distinguishes three different cases of friction:

Case (a). Very Smooth and Even Surface, Low Surface-Pressure.— The action is transmitted by intermediate bodies of microscopical size (Fig. 2, *a*). The area of surface of contact is, according to the formulas

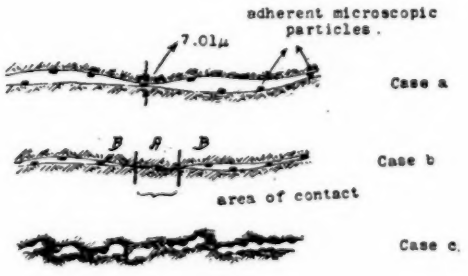

Fig. 2.

of Hertz, smaller the smaller the radius of curvature at the place of contact. Hence, as the shape of the intermediate bodies is a matter of chance, the coefficient of friction is extremely variable.

Case (b) Very Smooth and Even Surfaces, High Surface Pressure (Fig. 2, b).—The intermediate bodies disappear in depressions produced above and underneath them by high local pressure. The surfaces of the two main-bodies come in contact, the radius of curvature of this surface is by far bigger than the radius of curvature of the surfaces of the microscopical bodies, and the coefficient of friction goes rapidly up. With increasing pressure the peripheral parts *BB* of the surfaces whose radius of curvature is still greater than that of the central part *A* come in contact, the coefficient of friction increases therefore furthermore, although not as rapidly as at the limit between case (*a*) and case (*b*). These assumptions are verified by a series of facts published 1829 by Rennie.[1] This author found for the coefficient of friction f between steel and iron at different surface-pressures the following values:

Pressure $p = 8.79$ kg. cm.,$^{-2}$ $f = 0.166$ corresponding to a later stage of case (*a*).

$p = 23.62$ kg. cm.,$^{-2}$ $f = 0.333$, earlier stage of case (*b*).

With further increasing pressure p he found an increasing f until he obtained for $p = 47.25$ kg. cm.$^{-2}$, $f = 0.403$.

Experiments carried out with other materials led him to similar results indicating that the coefficient of friction rises first rapidly and then slowly with increasing pressure.

Case (c). Bodies with Rough Surfaces.—The friction is a complicated result of the effect of molecular attraction due to contact and of the fact that the asperities of the two surfaces stand to each other in a similar relation as the teeth of two gears (Fig. 2, *c*). But as the surface of contact is already at the very beginning more considerable than in case (*a*), as it can never reach as big values as in case (*b*) and as furthermore the second element which determines the frictional resistance in case (*c*), the geometrical form of the two surfaces, is practically independent of the pressure, the coefficient of friction is a fairly definite figure and this explains the curious fact that the complicated causes of friction between rough bodies lead to a simpler effect than the seemingly simple causes of friction between two smooth surfaces.

The indicated theory removes the apparent contradiction between the fact of tangential frictional force and the molecular theory of matter. As long as the surfaces are in contact they adhere to each other not only in tangential direction but in every other direction too. But the adhesion perpendicular to the surface cannot be observed because as soon as the pressure is relieved the area of contact becomes again nearly zero, the surface resuming their original shape and this remark leads to a very

[1] Phil. Trans., 1829.

important conclusion essential for the understanding of the properties of clays:

The ordinary laws of friction of rest are only applicable to the friction between bodies whose original surfaces do not fit each other and whose contact must be enforced by external pressure. Two bodies joining each other with perfectly even surfaces would present not only a lateral resistance against displacement but resistance against separation too.

The latter fact has been demonstrated by the following striking experiment: A very dilute solution of a clay, distinguished by the flat shape of its particles and very strong Brownian movements was placed on a thin sheet of glass, inside a ring of a height of 2 mm. Five minutes after having filled the ring, the cylindrical space was covered with a glass cover, so that there was no trace of air between the bottom and the cover, and the whole was turned upside down. Twelve hours later the vessel was turned again, and after another twelve hours top and bottom were examined under the microscope. All particles smaller than μ adhered to the glass cover and all particles bigger than this size stuck to the bottom. The colloidal particles showed no trace of Brownian movement, apparently kept in their position by molecular forces. Turning the vessel upside down again the coarse particles remained in their places on the upper surface of the water-body. A drawing was made of some characteristic parts of the crystal groups and twelve hours later it could be stated that no grain had left the top-cover, a clear proof, that in the case of contact without external pressure the retaining forces act not only in a horizontal but also in vertical direction.

The author is deeply indebted to the College and to Mr. Tubini, A. M. I. E. E., acting dean of the engineering department of Robert College for very liberal assistance.

Robert College,
Roumeli Hissar,
July 1, 1920.

SPEEDS IN SIGNALING BY THE USE OF LIGHT.

BY W. E. FORSYTHE.

SYNOPSIS.

Relative Length of Dot, Dash and Space for Light Signaling.—A preliminary investigation was carried out to determine the relative lengths of dot, space and dash necessary for the greatest speed. Three observers made readings for this test and all agreed very well with the following ratio for the maximum speed:

dot : dash : space :: 1 : 4 : 3.

Speed for Sharp Cut-off of Signals.—To test out the speed for a sharp cut-off of the signals, using this ratio for dot, dash and space, a sector was made with which seven different signals could be shown. This sector was mounted so that the observers saw the light source through a small opening. According to the criterion adopted, speeds were obtained that would correspond to 9 to 13 five-letter words per minute.

Speeds of Reading under Various Conditions.—It was shown that different observers were able to read the different signals at about the same speed with signals that were sharply cut off (as with the sector) and when the signals were made by turning on and off a special ribbon lamp filled with argon gas. The speeds of reading using other types of lamps were slower than for the ribbon lamp. With the observers at a distance and the lamp in a signalling unit, speeds somewhat slower were obtained. When an observer failed to read a given signal correctly the failure was generally due to his inability to see the dots.

IN connection with the design of some tungsten filament lamps to be used for signaling purposes it was found that little if any information was available as to the possible speed of signaling using flashes of light. This depends on two factors, the inertia of the eye and the characteristics of the source used. The purpose of this investigation was to ascertain if possible the maximum speed at which signals of this kind can be read and to compare this speed with those attainable when using certain types of tungsten filament signal lamps.

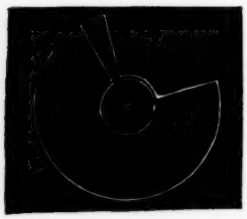

Fig. 1.
Disk with adjustable opaque sector.

A preliminary investigation was made to find the relative time intervals corresponding to a dot, space and dash which would permit of the maximum speed of reading. A disk was made up having a 120° opening and provided with a movable opaque sector which rotated with the disk (Fig. 1) but could be fixed at any position in the opening. The size of this sector determined the interval corresponding to a space while its

position defined the relative intervals for the dot and the dash. The speed of the disk was measured by a speedometer.

This disk was mounted between a lamp and a small opening (1.5 mm. in diameter) in front of which was placed a shutter controlled by a telegraphic key and relay, the latter connected with a commutator attached to the disk shaft. With the disk rotating, the shutter opened when the operator pressed a key, whereupon the observer, sitting about 4 meters in front of the opening, saw flashes of light of different duration with an intervening period of darkness and then the shutter closed. In this way a given signal was seen only once but by properly adjusting the position of the opaque sector it was possible to show any one of three signals, *i.e.*, dot space dash, dash space dot, or dash alone. Using a given size of sector and a given ratio of dot to dash interval, a number of these signals given in irregular order were presented for successively increasing speeds of the disk until a speed was reached beyond which they could no longer be differentiated. Then using the same sector, the ratio of the dot and dash intervals was changed and another series of readings was made until the maximum speed was reached. From the data thus obtained a curve was plotted with the ratio of dash to dot as abscissa and for ordinate the reciprocal of the time required to see the

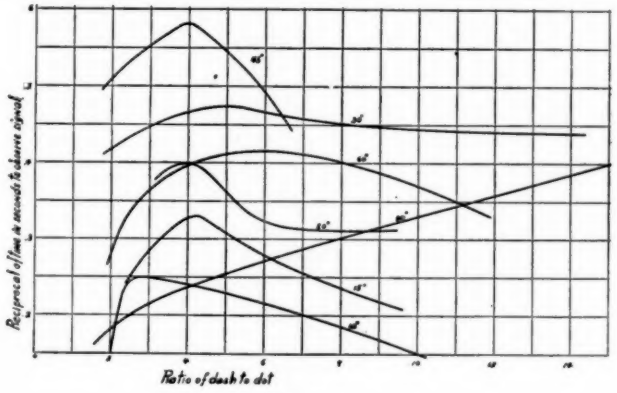

Fig. 2.

complete signal when the disk was rotated at a maximum speed. The procedure was repeated for a series of seven different sized opaque sectors, subtending angles of 10°, 15°, 20°, 30°, 45°, 60°, 80° and thus a family of curves was obtained as shown in Fig. 2. They represent the observations of a single observer, and show that for this observer and under the given conditions a ratio of dash to dot of approximately 4 to 1 corresponded to the maximum speed of reading for most of the sectors and particularly for the 45° sector. Moreover the speed using the latter sector was greater

than that obtained with the 30° on the one hand or the 60° on the other, and hence the correct size of sector for the greatest attainable speed would seem to be in the neighborhood of 45°. This corresponds to a proportionality of dot : dash : space :: 1 : 4 : 3. Later, a like test by another observer gave results slightly different from those shown in Fig. 2. The maximum speed when the movable sector was 45° occurred for a ratio of dot to dash of about 1 : 4 as in the first test. In this second test, observations were made with a 52½° sector and the value for the maximum speed was about equal to that for the 45° sector, with the difference in this case, however, that the ratio of dot to dash for maximum speed was about 1 : 9, which gives 1 : 8 : 9 as the proportionality for dot, space and dash.

This second test seemed to show that about the same maximum speed would be obtained for the sectors above 45° up to 80° out of 120, with the difference, however, that there was a very great increase in the ratio of dot to dash for the very large sectors.

It is well known that in the case of any incandescent electric lamp a time interval elapses after the current is turned on before the filament glows with full brilliancy, and similarly time is required for the glow to disappear after the current has been cut off. If it were possible to construct a lamp in which full brilliancy and complete absence of glow were synchronous with the closing and opening of the circuit it would be possible to study the part played by the eye in determining the maximum speed of signaling independent of the characteristic of the lamp. Such a limiting case can be almost exactly reproduced by the use of a disk with proper openings rotating in front of a very small opening before a continuously luminous source. The relative time intervals for dot dash and space found in the preliminary investigation evidently apply rigorously only to this limiting case, and it should be noted that while the use of this proportionality for any signal lamp is an assumption, it is probably not far from right and applies to all of the data to be subsequently presented.

In the main experiment the first procedure was designed to ascertain the maximum speed of signaling for the limiting case, and to compare this with that obtained when the flashes were produced directly by a type of signal lamp which other experiments indicated would give the greatest speed. The previously mentioned disk might have been used for this purpose but in order to have a greater number and more complicated signals corresponding more nearly to those used in practice, a second disk was constructed using the ratios noted above for dot, dash and space. It is illustrated in Fig. 3 and with it the following seven

signals could be shown (a space of course occurs after each dot and each dash):

1 dot dash dot dash
2 dash dot dot dash
3 dash dot dot
4 dash dot dash dot
5 dash dash dot dot
6 dot dash dash dot
7 dot dash dash

This disk was then mounted with respect to the signal lamp in a manner quite similar to that described for the disk used in the preliminary experiment. The apparatus was so arranged that the different signals could be presented in any prearranged order while the disk was in rotation. The position of the observer and the use of the shutter were the same as previously described. A 6-volt, 2-ampere ribbon-filament signal-type tungsten lamp was used as a source, and held at a color temperature in the neighborhood of 2950° K. The intensity of the light was so great that a one per cent. transmission screen was interposed to make observation more comfortable. The intensity was still ample for accurate reading.

Fig. 3.

Disk with open and closed spaces to give seven different signals.

The following method was employed in making a test. A series of 12 signals arranged in a haphazard order as determined by the playing-card method, were presented at each of a series of successively increasing speeds of the disk, starting at a point such, that there was no question of ability to decide what the signal was. A record was made of all decisions and the experiment was continued until a speed was reached at which, from the number of errors, it was evident the observer had passed the limit of accurate judgment.

In order to make measurements with the lamp directly, a commutator was constructed by means of which the intervals during which current was turned on and off were in the same ratio for dot, space and dash as the disk-exposure times previously referred to. The relation of dot : space : dash is somewhat different in this case than when the sector was used. This is due to the fact that it takes a somewhat longer time for a lamp to heat up than to cool off. This shortens the dot relative to the dash and lengthens the space. From the results of the test for the relative length of dot to dash by the second observer, this would make but little difference, if any, in the final results. With the disk removed but

other arrangements the same, an exactly similar series of readings were made as before, using the 12 signals and successively increasing speeds. There was practically no resistance in series with the lamp. Each observer made runs with both the disk and the lamp, the two series of measurements following each other in rapid succession in order to maintain as nearly as possible the same eye conditions.

The results are shown in Table I. In column one are given the reciprocals of the time in seconds from the beginning to the end of the signal. In the succeeding columns are given for each observer the number of

TABLE I.

Results for Disk Compared with those for Ribbon-Filament Tungsten Lamp in Argon.

Reciprocal of Time in Seconds from Beginning to End	Number of Signals Read Correctly Out of the Twelve Signals Shown.					
	W. W.		J. R. C.		F. E. C.	
	Disk.	Lamp.	Disk.	Lamp.	Disk.	Lamp.
.20	12	12	12	12	12	12
.25	12	12	12	12	12	12
.30	12	12	12	12	12	12
.35	12	12	12	12	11	11
.40	11	12	12	12	11	11
.45	10	12	11	12	11	10
.50	10	12	12	12	9	10
.55	9	12	12	12	9	9
.60	9	11	12	12	7	7
.65	8	8	12	12	4	7
.70	8	11	12	11	5	9
.75	7	9	11	10	6	3
.80	5	5	12	10	3	7
.85	7	5	7	9	6	3
.90	3	3	9	5	1	5
.95	4	1	5	0	0	3
1.00			4			4

The results for W.W. indicate a breakdown at about the point .50 which corresponds to a speed of about 9 five-letter words per minute.

For J.R.C. the breakdown point would be at about .80 which corresponds to a speed of 13 five-letter words per minute.

The results are arrived at by allowing two mistakes out of the twelve signals shown.

signals read correctly out of the 12 presented at each speed, both when the disk was used and when the lamp was used directly with the commutator. The data show very little if any difference on the average between the results using the disk and those using the lamp and indicate that the eye and not the lamp was the limiting factor in the speed of reading the signals.

Having found that the special gas-filled ribbon-filament tungsten lamp

used gave results as good as those obtained by the use of the disk, it seemed desirable to compare this lamp with other equivalent types such as a lamp with a ribbon filament, in a vacuum, and also a gas-filled wire-filament lamp. The previous tests were all carried out in the laboratory where the observer was insured plenty of light and sharp contrast and had no difficulty in locating the flash. In order to carry on the tests under conditions more nearly like those which occur in practice, the lamp and commutator apparatus were moved up to the roof of the laboratory. The effect of distance between the observer and the apparatus was simulated by setting up the lamp without a reflector so that the observer saw the flash, against the sky as a background, with an intensity such as to give a flux equivalent to that which would be obtained by the use of the regular reflecting apparatus with the observer 20 or 30 times as far away. The procedure as to number and order of signals and speeds was the same as before. In the first test comparison was made with a lamp having a ribbon filament of the same shape but in a vacuum. The lamps were oriented so that the intensity in the direction of the observer was the same for each. For this run the observer was stationed at a distance of 100 yards and the results, given in the second and third columns of Table II. indicate that the gas-filled lamp is best for this work. A comparison was then made of the gas-filled tungsten-

TABLE II.

Comparison between a Gas-filled Ribbon Lamp and a Vacuum Ribbon Lamp; also between a Ribbon Lamp and a Wire Lamp, both Gas-filled.

Reciprocal of Time in Seconds from Beginning to End of Signal.	Number of Signals Read Correctly Out of the Twelve Signals Shown.							
	W.W.		J.R.C.		W. W.		K.M.	
	Gas-filled Ribbon[1] Lamp.	Vacuum Lamp.	Gas-filled Ribbon Lamp.[2]	Gas-filled Wire Lamp.	Gas-filled Ribbon Lamp.[2]	Gas-filled Wire Lamp.	Gas-filled Ribbon Lamp.[2]	Gas-filled Wire Lamp.
.20	12	12	12	12	12	12	12	10
.25	12	12	12	11	12	12	12	11
.30	12	11	12	12	12	11	12	5
.35	12	8	11	6	12	11	10	
.40	11	8	9	8	9	9	8	
.45	12	7	6		8	6		
.50	9	7	7		8	7		
.55	8	6			7			
.60	5	2			5			
.65	6							
.70	3							

[1] Distance of observer 100 yards.

[2] Distance of observer 170 yards.

ribbon lamp and a gas-filled tungsten-wire lamp using three observers at a distance of 170 yards. The former lamp was run at a color temperature of about 3000° K. and the latter at about 3100° K. As before the lamps were oriented so as to have approximately the same intensity in the direction of observation, and the results indicate superiority for the ribbon type. As operated for the most part in this test there was some

TABLE III.

Determination of Speed of Signalling under Various Atmospherical Conditions and at a Distance of 2,700 Yards with a Gas-filled ribbon-filament tungsten signal lamp mounted in a Standard Housing with a Reflector.

Reciprocal of Time in Seconds From Beginning to End of Signal.	Number of Signals Read Correctly Out of the Twelve Signals Shown.						
	1.	2.	3.	4.		5.	6.
			Results of W.W.				
.15	11			12	10		
.20	12			12	12	12	
.25	12	12	12	11	11	12	12
.30	11	11	11	12	8	12	12
.35	12	9	12	12	9	12	12
.40	12	8	11	11	7	12	12
.45	9	6	9		7	12	11
.50	11	6	7		9	11	12
.55	7	7	6		8	12	10
.60	8	4	6			9	5
.65	5	5	4				5
.70	5		4				4
.75	7	3	4				
			Results of K.M.				
.15	11						
.20	12			12	9		
.25	12	12	12	12	12	12	
.30	11	11	11	12	9	11	12
.35	12	12	7	12	9	11	12
.40	9	11	10	11	10	12	12
.45	7	10	5	12	7	10	11
.50	9	7	8		6	5	11
.55	8	6	8		6	0	12
.60	7	3	8		5	0	11
.65	0	0	7				5
.70							4
.75							0

1. Cloudy, conditions changing.
2. Cloudy, some fog.
3. Cloudy, some fog.
4. Clear day.
5. Clear day.
6. Night.

resistance in the lamp circuit. The effect of this should be to lower the speed of the lamps. A test to see whether the effect would be appreciable and different in the two lamps showed a slowing up in both but a difference so small as to be almost within the limits of experimental error.

To still further reproduce actual practice two observers were placed at a distance of 2,700 yards. The gas-filled ribbon lamp was then placed in a regular signaling unit which gave about a 5-degree spread. The data are recorded in Table III. For observer *WW*, the limit of speed of receiving signals would appear to be lower on foggy days than on clear days and highest at night. On the other hand the results of K.M. showed little difference on clear or foggy days, but were better at night.

Assuming a five-letter word, and that the same speed was maintained for continuous sending of signals the 0.50 point in column one corresponds to about 9 words per minute, and the 0.80 point to about 13 words per minute.

A word might be said regarding the appearance of the signals when the speed approached the limit beyond which the signals could not be identified. Each observer was instructed to record what he saw, not by code letter, but by actually writing down the dots and dashes. A study of these records shows that on clear days inability to see initial dots caused uncertainty and eventually breakdown, dashes only being seen ultimately. At night, owing to the greater apparent brightness, the spaces seemed to vanish and a mere flicker appeared. In this connection it should be noted that in night work no red glasses were used such as are frequently employed in practice.

Nela Research Laboratory,
Cleveland, Ohio,
March, 1920.

PHENOMENA IN OXIDE-COATED FILAMENT ELECTRON TUBES.

BY H. D. ARNOLD.

SYNOPSIS.

Thermionic Phenomena in Wehnelt Oxide Electron Tubes.—The author discusses some of the problems which have arisen in connection with the development of three-electrode vacuum tubes with special reference to the production of a highly active and uniform thermionic source of electrons. The materials and the methods for the preparation of both core and coating are given. Since tubes with these filaments are not self-evacuating by the clean-up effect to the extent found with tungsten filaments, greater care is necessary in the pumping process.

Pure Electron Discharge; the Influence of Pressure and of Bombardment by Positive Ions.—The evidence shows the electron emission from Wehnelt oxides to be purely thermionic. Preliminary measurements on the number of electrons emitted from these filaments under the bombardment of positive ions prove that no appreciable part of their activity can be attributed to this cause. Operation has been studied with pressures of the order of 10^{-10} mm. Hg., but no decrease in activity is found at these low pressures. A plot is given summarizing the constants of Richardson's equation for 4,000 filaments.

Rate of Evaporation of Oxide Coating.—Grams per cm.^{2} per sec. evaporated from a filament coated by the above process are approximately given by

$$m = 4.6 \times 10^8 T^{-1/2} \epsilon - \frac{4.6 \times 10^4}{T}.$$

Thinly Coated Filaments; Coating by Evaporation.—Preliminary results of work now being carried on by Dr. C. J. Davisson show that maximum thermionic activity may be reached with coatings considerably less than one molecule deep. This suggests that of the two important constants determining electron emission, the density of free electrons in the substance and the work function at the surface, the latter is modified by the presence of the oxides while the former may remain essentially that of the core.

THE most generally interesting phenomena in electron tubes are those relating to the flow of electrons through the space, the control of this flow by plate and grid voltages, and the operation of the tubes in the various circuits in which they are used. These phenomena are essentially the same whether the filament is pure metal or is oxide coated, and a considerable literature has already grown up in this field. The phenomena distinctive of oxide-coated filament tubes are those relating to the economic and scientific factors involved in the process of electron emission. I shall therefore confine myself as closely as possible to these factors as they have influenced the design of oxide filament tubes,

and as we have been led to investigate them in connection with our development of these tubes during the past seven years. For reference to the scientific literature in this field attention is called to the appended bibliography.

Wehnelt oxide filaments offer the most economical source of electrons at present available for use in three-electrode vacuum tubes, and thus from a commercial point of view they are at present of the greatest interest and importance. On purely scientific grounds they have long been of peculiar interest to physicists and chemists, offering as they have one of the most promising fields for speculations on the possible effect of chemical action in aiding the emission of electrons from hot bodies.

The early work of Richardson, H. A. Wilson, and others, established beyond reasonable doubt that for pure metals the emission of electrons is due to thermal action and not to chemical action in the ordinary sense of the word. Of the early evidence the most convincing was the proof that the emission did not decrease as more and more of the residual gas was removed, and the proof that the emission did obey the law of variation with temperature which would be expected if the effect were purely thermal. Further work[1] showed that the distribution of velocities among the emitted electrons was that which would be computed on the basis of the equipartition of energy between molecules and free electrons in the metal, the faster of the free electrons escaping in spite of the restraining influence of an electric field at the surface of the metal. Still other experiments[2] established that the value of this potential difference, as determined from the cooling of the metal due to the electron emission, corresponded with the value deduced from the observed relation between emission current and temperature. In view of these facts physicists have believed for the past ten years or more that there was no place for a chemical theory of emission as far as pure metals are concerned.

With respect to Wehnelt oxides, however, there was somewhat less certainty as to whether chemical action might not be necessary for electron emission. While it is true that early experiments established that with oxides as well as with pure metals the emission did not depend on the presence of gas in the evacuated chamber, the presence of the oxide itself on the filament seemed to offer sufficient chance for chemical actions, irrespective of any gas. Moreover, the fact that coating metals with these chemical compounds increased their electron emission many fold seemed to invite the hypothesis that this increase resulted from

[1] Richardson and Brown, Phil. Mag., Vol. XVI., p. 353 (1908).

[2] Richardson and Cooke, Phil. Mag., Vol. XXV., p. 624 (1913); Vol. XXVI., p. 472 (1913)

chemical action, although there has never been any experimental evidence clearly requiring such an hypothesis.

Data similar to those which established the purely thermal nature of thermionic emission from metals, were accumulated more slowly in the case of Wehnelt oxides, largely because of experimental difficulties which were encountered. The determination of the correspondence of the work function as obtained from the cooling effect, and as found from the exponent in the emission-temperature equation, followed several years behind the similar determination for pure metals, this in spite of the fact that the earliest experiments with the cooling effect were attempted by Wehnelt and Jentzsch[1] using Wehnelt oxides. As for the velocity distribution among the emitted electrons, this, as far as I am aware, has still to be satisfactorily determined for the oxides. Nevertheless, the evidence as it has been verified step by step has in every case supported the opinion of the physicists who believed that emission from oxides as well as metals was in all probability a purely thermal affair and did not require any assumption of chemical action for its explanation.

With the inception of the use of oxide filaments for commercial vacuum tubes, we had to face the same difficulties of technique in producing the filament that had retarded the scientific experimenters in their work, and it was in addition necessary to produce filament in large quantities and with a very high degree of uniformity. To do this a survey was made of the metals available for the core of the filament, and of the materials and methods of coating best adapted to the manufacture of a highly active and uniform filament. Considerations of mechanical strength, electrical resistance, non-oxidizability, availability and reproducibility of commercial supply, etc., led us to choose for the core a wire of platinum-iridium (about six per cent. iridium, with the other impurities usually found in commercial platinum-iridium). This wire was rolled to a ribbon to increase the surface, and the ribbon was twisted to secure a better mechanical structure. This core could be produced in quantity with electrical and mechanical properties sufficiently uniform for our purpose.

In the choice of coating materials we had available the oxides of barium, strontium, and calcium, with thermionic activities in the order given. Experiments with coatings of BaO, however, showed a mechanical disintegration during life which outweighed in importance its superior thermionic activity. Efforts to secure longer life resulted in the use of a mixture of BaO and SrO applied in a number of consecutive coatings.

[1] Wehnelt and Jentzsch, Verh. der Deutsch. Physik. Ges., 10 Jahrg., p. 610 (1908); Ann. der Physik, Vol. XXVIII., p. 537 (1909).

In the process which we most commonly used, barium in the form of carbonate, and strontium in the form of hydroxide or carbonate, was mixed with some carrier such as resin or paraffin, which would burn away when heated in the air. In the coating process four applications of the strontium mixture were followed by four of the barium mixture, and this process was then repeated, making a total of sixteen separate applications. After each application the wire was raised momentarily to a temperature of about a thousand degrees, which burned away most of the organic carrier. When the coating was complete the wire was heated to about 1200° for two hours. At the end of this time there remains a fairly heavy coat of BaO and SrO (from 2 to 3 milligrams per sq. cm. surface), while next to the core is a firmly adhering layer which is built up due to chemical reactions between the coating and the core. Analysis shows this coating to consist of barium and strontium combined with platinum, rhodium and iridium, the compound present in largest amount being barium platinate ($BaPtO_3$). The compound with rhodium seems to be more readily formed, but due to the small percentage of rhodium present this compound makes up only a small fraction of the total.

The filament thus formed can be handled without undue precaution so long as it is not exposed to moisture or carbon dioxide. When stored in vacuum containers it shows no signs of deterioration even after a period of several years.

The time required for the proper evacuation of an oxide filament tube is determined almost entirely by the requirement that a large part of the occluded gases must be removed from the metal and glass parts inside the bulb. In case the metal parts can be heated before assembly, or can be heated electrically, either through leads from the outside or by Tesla currents, the evacuating process may be very much shortened. In any event it is desirable to carry the evacuating process considerably further in the case of oxide filament tubes than with tungsten filament tubes, since the clean up effect of the filament itself is not nearly so marked as is the case with tungsten.

During the pumping process the filaments are glowed for several minutes to liberate any gases they may have occluded. At the same time the compounds at the surface of the core decompose to a certain extent, as is evidenced by the fact that filaments taken from tubes after a considerable period of glowing show a marked diminution in the amount of $BaPtO_3$ and similar compounds.

With the exercise of proper care as to the purity of the materials used and with adherence to a definite schedule of coating and heat treatment,

filament can be produced with every expectation of uniformity and long life. During the war some half million vacuum tubes were made employing this filament, and the filament was prepared as a part of the regular manufacturing process by practically unskilled labor. Expert supervision was of course necessary to guard against the intrusion of chemical impurities or variations in the coating process.

We have naturally made a very thorough study of this so-called "standard" filament in order to determine its properties and particularly the factors which influence it during life. Having been developed in the first instance, about seven years ago, to meet the needs of telephone repeater service, severe requirements were imposed upon it from the start. Tubes made with it are required to be completely interchangeable. No adjustment of filament or plate voltages is made when tubes are replaced, and no appreciable change in amplification, or in electron current, may result from an interchange. The operation of the tube as an amplifier must remain unchanged when the filament voltage is varied between the limits customarily met with in storage battery service. The operation of the tube must remain sensibly unchanged through a life of several thousand hours, and when it does fail for any reason, it must give sufficient warning to ensure its being removed from service without causing the interruption of a telephone conversation. These and numerous other requirements are rigorously enforced, making it far more difficult to manufacture tubes for telephone repeater service than for the other uses for which they have since been adopted.

What terminates the useful life of an oxide filament is usually the development of local faults or "bright spots" due to the evaporation of the coating. They are practically free from the most common ageing effect of pure metal filaments, namely the gradual increase of electrical resistance caused by the evaporation of the filament. In the case of tungsten filaments used on constant voltage supply evaporation with the resulting increase in resistance causes a lowering in the filament temperature and therefore a decrease of the electron emission, while with a constant current supply the increase in resistance results in an increase of temperature and a progressive increase in rate of disintegration of the filament. With oxide coated filaments it is the coating alone that evaporates, at least until a bright spot is formed, and the temperature and operating characteristics remain unchanged throughout life on either constant current or constant voltage supply.

The cost of electrons in a vacuum tube device is determined by the characteristics of the filament, by the cost of the power used in heating the filament, and by the life and the replacement cost of the tube. The

physical factors necessary for computing the cost are the constants in Richardson's equation, the constants of the evaporation equation, and the radiation constant peculiar to the filament. In order to relate the life of the tube to the vaporization constants it is necessary in addition to know to what extent vaporization may proceed, on the average, before the useful life is terminated, and this can, of course, only be arrived at by exhaustive life tests.

For tungsten and molybdenum the physical constants are already available, but for Wehnelt oxide filaments these constants have not as yet been satisfactorily established. Preliminary results have, however, been obtained in our laboratory and Dr. C. J. Davisson is continuing the investigation. We have found that the total thermal emissivity lies between 0.45 and 0.70, for a considerable number of samples of our standard filament. The method followed in determining these limits was to get the resistance power relation for the filament under operating conditions, and later get the resistance-temperature relation by placing the tube in an electric furnace. The latter relation was checked by an observation at the melting point of potassium sulphate. In connection with measurements of filament temperatures it was found by the use of the optical wedge method that these oxides act practically like black bodies in the red region of the spectrum and hence the temperature can be read with a fair degree of accuracy by means of an optical pyrometer using the black body calibration.

The preliminary values of the evaporation constants, obtained by evaporating barum oxide from a tungsten boat, catching it on a platinum shield, and weighing the deposit show that with a fair approximation

$$m = 4.6 \times 10^8 T^{-1/2} \epsilon^{-[(4.6\times 10^4)/T]},$$

where m is the rate of evaporation in grams per sq. cm. per second. A more definite determination of these constants for BaO, SrO and CaO is under way.

As for the determination of the constants in Richardson's equation for oxide filament, this work has covered about 4,000 filaments, and the results are of sufficient interest to warrant more detailed consideration. To simplify the investigation of this matter Dr. Davisson has devised a form of coördinate paper in which the coördinates are power supplied to the filament (abscissæ) and thermionic emission (ordinates). The coördinate lines are so disposed and numbered that if the emission from a filament satisfies Richardson's relation, and the thermal radiation satisfies the Stefan-Boltzmann relation, then points on the chart coordinating power and emission for such a filament will fall on a straight

line. For practical purposes the advantage of replacing temperature by power as the independent variable is obvious. From the slope and position of a line on this chart together with the area of the filament, it is possible to calculate $bE^{1/4}$ and $aE^{-1/8}$ where b and a are Richardson's constants and E is the total thermal emissivity of the filament. The lines shown in Fig. 1 give some idea of the characteristics of our standard

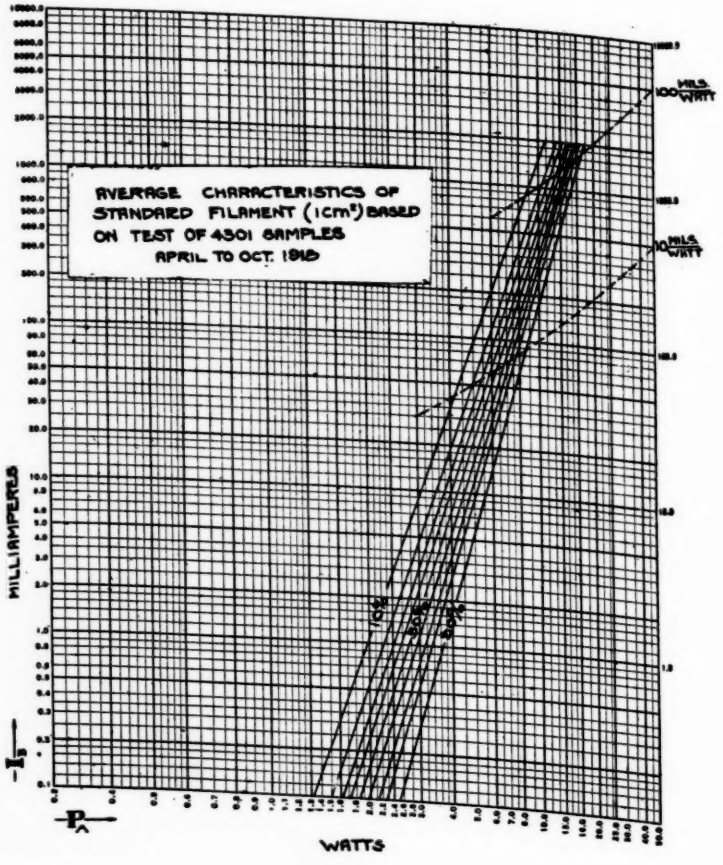
AVERAGE CHARACTERISTICS OF STANDARD FILAMENT (1cm²) BASED ON TEST OF 4501 SAMPLES APRIL TO OCT. 1915
MILLIAMPERES
WATTS
100 MILS WATT
10 MILS WATT

Fig. 1.

filament and the range of variability. Ten per cent. of the filaments have a greater activity than that given by the upper line while the activity for 90 per cent. of the filaments lies above the lowest line. In this connection it should not be overlooked that in the great majority of vacuum tube applications we are concerned only in maintaining the electron emission at a value greater than a certain fixed limit. It is in no way injurious for the emission to exceed this limiting value. In a limited number of cases, however, it is desirable to use tubes with as

nearly as possible the same voltage saturation value of emission. For these special problems pure metal filaments offer at present the best solution, since the uniformity of their saturation values can be more readily maintained.

The dotted curved lines on the figure are drawn through points of constant ratio of emission to power, that is, constant efficiency or economy. The customary operating power is from 8 to 9 watts per cm.^{2}, so that the range of efficiencies is seen to lie between 10 mils per watt and 100 mils per watt. Assuming the emissivity of the filament to be 0.6 we obtain from these lines the following values of thermionic characteristics of the filament.

Equivalent volts through surface $\phi = 1.55$ to 1.9,

Richardson's constant b, 19.4×10^3 to 23.8×10^3,

Richardson's constant a, $(0.5 \text{ to } 1.5) \times 10^{24}$ for electrons per sec. per cm.^{2},

$(8 \text{ to } 24) \times 10^4$ for amps./cm.^{2}

In our adaptation of Wehnelt oxide coated filaments to commercial vacuum devices we have found it desirable in a number of instances to carry on investigations which would appear to be more immediately of scientific than of commercial value. One of our early experiments which was reported by Dr. W. Wilson at the Christmas meeting of the American Physical Society in 1914 gave additional data as to the behavior of Wehnelt oxide filaments in very high vacuum. The experimental arrangement used consisted of a cylindrical anode, with suitable guard rings, surrounding a single strand of oxide coated filament placed along the axis of the cylinder. The vacuum was made as good as possible with a Gaede molecular pump and it was established that the electron current in the filament did not diminish even with these extreme vacua. It was expected that the current would vary with the 3/2 power of the voltage according to Child's[1] space charge relation and that from the coefficient K, which involves among other factors the quantity $\sqrt{e/m}$ we might determine whether the carriers in the case of Wehnelt oxide filament were electrons or were in part carriers of greater mass. Wilson found that when proper consideration was taken of the geometrical form and of the voltage drop along the filament, the space charge equation took the form[2]

$$i = k\frac{2}{5}\frac{(V - V_0')^{5/2}}{V_0 - V_0'}\left[1 - \left(1 - \frac{V_0 - V_0'}{V - V_0'}\right)^{5/2}\right],$$

[1] Child, PHYS. REV., Vol. 32, p. 492 (1911).

[2] See also E. R. Stoekle, PHYS. REV., Vol. VIII., p. 545 (1916).

where V_0' is the potential of the negative end of the filament and V_0 the potential of the positive end. The value e/m obtained from the experimental data by the use of this equation was found under the best conditions to be about 5 per cent. lower than the value obtained for electrons by other methods. This deviation is explicable either by the presence of a very small number of negative carriers of molecular size or by the emission of secondary electrons from the anode under the bombardment of the primary electrons. The deviation is however, no greater than that obtained with tungsten filaments, and the concordance of the results indicates clearly that the discharge from Wehnelt oxides may be considered a pure electron discharge.

By means of the Knudsen absolute manometer, and later by the use of the Buckley ionization manometer,[1] we have measured vacua of the order of 10^{-9} and 10^{-10} millimeters of mercury during the operation of Wehnelt oxide filaments, and have never found any indication of the emission current falling off as the vacuum improved. With the introduction of various gases at pressures of the order of .001 millimeter, or so, the electron emission currents do suffer rather large changes, although not of the degree found with the emission from tungsten filaments under similar conditions. The presence of oxygen and carbon dioxide inhibit the electron emission, while a small amount of hydrogen in contact with a filament of abnormally low emission may result in restoring it to a normal condition. Because of their relatively smaller variations in emission under the action of gases we have found Wehnelt oxide filaments more adaptable for use in Buckley ionization manometers than pure metal filaments, as it is very rare that any blocking effects develop which cannot be overcome by a reasonable increase in the filament temperature.

In another paper[2] before the Physical Society in April, 1917, Wilson gave the results of a series of experiments on the relation between the work function ϕ and the exponent b of Richardson's equation. The method followed was a modification of that first attempted by Wehnelt and Jentzsch for oxide filaments and later used by Richardson and his collaborators in investigating the cooling effect due to the emission of electrons from filaments of osmium and tungsten. Previous experimenters who had attempted to determine the cooling effects with Wehnelt oxides had found it impossible to get consistent results due to the non-uniform behavior of the filament. During Wilson's experiments our standard methods of coating were employed, and the results obtained were remarkably consistent and reproducible. The values obtained were as follows:

[1] O. E. Buckley, Proc. Nat. Acad. Sci., 2, 683 (1916).

[2] Proc. Nat. Acad. Sci., 3, 426 (1917).

	bR/e Volts.	ϕ Volts.
BaO 50 per cent., SrO 50 per cent.	2.02	1.97
	2.16	2.28
BaO 50 per cent., SrO 25 per cent., CaO 25 per cent.	2.34	2.39
	2.59	2.54
CaO	3.28	3.22
	3.49	3.51

We have recently been repeating some of these experiments with a slightly different bridge arrangement and find no difficulty in obtaining consistent results from a given filament over long periods of time.

The close correspondence between b and ϕ, is as pointed out above, one of the grounds for believing that chemical action does not play any part in thermionic emission. The correspondence is, of course, not a proof of the absence of chemical action, but it is certainly more easily explained on the assumption of thermal action than on the assumption of chemical action. The determination of ϕ is also of considerable importance in connection with the theory of photo-emission and of contact potentials.

In connection with our recent experiments Dr. Davisson is finding it of great convenience to use filaments which have been coated by active material evaporated from a standard filament. The standard filament and the wire to be coated are mounted close together in the same tube and the primary is run at a fairly high temperature for various lengths of time according to the purpose of the experiment. Observations are then made on the emission from the secondary filament. One advantage of this method of experimentation is that the core of the secondary filament may be any suitable material, for example, tungsten or iron, without meeting the difficulties of oxidation, which are often troublesome when these materials are coated in the open air.

These secondary filaments have many interesting properties which no doubt will prove of importance in establishing the process of electron emission from Wehnelt oxides. One of the most striking facts is that the secondary filament may show a high electron emission when only a very minute amount of active material has been transferred to it. In certain experiments where the secondary filament was tungsten, the standard filament was glowed for so short a time that only approximately one tenth of the surface of the tungsten filament was covered with active material. While we have not determined in just what form the deposit comes down on the secondary, it seems reasonable to suppose that the material is transferred essentially molecule by molecule, and that the surface of the secondary filament would be found to have on it a consider-

able number of single molecules of coating separated by distances of the order of one to ten molecular diameters, and in addition a certain number of groups of two molecules, a much smaller number of groups of three molecules, and so on. It is most interesting to note that the electron current obtainable at a given temperature from filament coated in this very tenuous fashion may be only a little smaller than that obtained when the entire filament is covered with a heavy deposit.

It is natural to ask whether this result is due to a difference in the a or in the b of Richardson's equation as applied to these partly coated filaments. Work along this line is not yet completed, but measurements of b taken at intervals while the deposit was forming have never shown an increase with thickness of deposit, and therefore it seems that the result must be due to a difference in a. If we assume that a completely coated filament emits uniformly over its entire surface, while a partly coated filament emits only in the vicinity of the molecule of active material, we compute an a for the partly coated filaments which is much greater than the values (0.5×10^{24} to 1.5×10^{24}) given above for standard filament. The fact that the b obtained for filaments coated merely with a few widely separated molecules is the same as that obtained with a complete coating shows that the reduction of the work function at the metal surface can be brought about by a very small group of molecules. Under these conditions it seems reasonable to suppose that the only important effect of the molecule of active material is to lower the restraining voltage in its own vicinity and thus facilitate the passage of electrons from the metal core. The number of electrons that can avail themselves of such a molecular opening is limited to those presenting themselves with a sufficient outward velocity, and this in turn is determined by the properties of the core material. Since the core materials used have values of a greater than those which we find for the standard filaments it does not seem so strange that the values of a for the partly coated filaments should be found to run higher than those for completely covered filament.

We hope that our present experiments will throw more light on the factors involved in the escape of electrons through these minute activated areas. Our information is at present too meager to warrant an opinion as to whether an electron on its way out remains for some time as a part of the molecule of active material or merely slips past it. The number of electrons passing out through one molecular opening in a second may be of the order of ten thousand, and that this rate may persist for some time is indicated by the rather slow rate of decay of activity. This proves at least that no irreversible chemical change in the active coating is involved in the emission of an electron. Perhaps a more

striking proof of this is found in certain of our filaments which through a life of twenty thousand hours have emitted fifteen times more mass of electrons than the mass of their coating.

Another factor of considerable importance in connection with the use of Wehnelt oxides is the facility with which they emit electrons when bombarded by electrons or by positive carriers. The factors governing the emission of secondary electrons are not well understood even in the case of pure metals. Experiments which we have performed with redistilled mercury surfaces indicate that the secondary emission may become very small when an absolutely clean surface is obtained. With Wehnelt oxides the secondary emission may be comparatively large, several electrons being liberated by each one that strikes the surface. Under the bombardment of positive carriers, however, secondary electron emission does not appear to take place so readily, and our experiments have not as yet shown evidence of more than a few electrons emitted per impact. This negatives the idea, which a few people have held, that positive ion bombardment is a controlling factor in electron emission from oxide coated filaments.

In conclusion, it may be remarked that while oxide coated filaments, under the pressure of necessity, have been developed to the state where they can be manufactured and used on an immense commercial scale as evidenced by their employment in more than half a million vacuum tubes, and while they easily hold the field as the most economical, and longest lived, source of electrons available for electron tube devices, we have not as yet by any means reached the limit of their possible development. The physical constants delimiting the operation of pure metal filaments are well known for the metals now available, and there is no apparent avenue by which their efficiency can be materially increased. Marked advance can only be expected when we depart from pure metals by mixing or coating them with other materials. In the case of the oxides, which at present furnish the best material for coating, it is not at all unusual to find sporadic cases of enormously greater activity than the average which we obtain by commercial coating processes. The limit to which improvement may be expected to extend can only be determined when the factors governing electron emission from the oxides are as well understood as are at present those governing electron emission from the pure metals. It is more than probable that in the process of obtaining this knowledge about the oxides we will find new light thrown upon the process of emission from pure metals as well.

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NOTE ON THE END CORRECTION IN THE DETERMINATION OF GAS VISCOSITY BY THE CAPILLARY TUBE METHOD.

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SYNOPSIS.

Assumptions Underlying Fisher's Formula for the End Correction.—Experiments by Benton having pointed to the conclusion that Brillouin's formula for the end correction represents the facts fairly well, whereas Fisher's does not hold even approximately; the writer points out that the experimental conditions assumed in the two formulas are essentially different. The use by Benton of comparatively short tubes with square cut ends gives a turbulent condition at the ends similar to that assumed by Brillouin, whereas Fisher assumes a slow stream-line flow such as could be attained only by the use of long tubes with gently tapered ends. The conclusions reached by Benton are therefore to have been expected.

IN reply to the note by A. F. Benton (PHYS. REV., 14, p. 463, 1919) "On the End Correction in the Determination of Gas Viscosity by the Capillary Tube Method," it may be said that the approximate formula for kinetic pressure drop proposed by me (PHYS. REV., 32, p. 216, 1911) is based on the following suppositions:

1. Such a low speed in the tube that the stream lines within are all parallel to the axis and expansion of the gas does not result in change in temperature, the necessary heat being supplied by conduction through the tube walls;

2. Both ends of the bore so gently tapered that the gas stream flows without anywhere leaving the glass; so that from stationary gas in the high pressure reservoir to stationary gas in the low pressure reservoir there is continuous stream line flow without turbulence.

Unfortunately neither of these conditions was explicitly stated in my note, though both clearly underlie the use made of Boyle's law and Bernoulli's theorem. I regret that my obscurity in expression should have led Mr. Benton to apply a correction formula in an experimental case to which its theory is entirely inapplicable; for the emergent jet from a square ended tube of diameter not small in proportion to its length is surely an illustration of stream line flow, and expansion within such a tube is known from published experimental data to be anything but isothermal; there is a decided temperature fall along such a tube, very pronounced as the exit is approached.

The correction formula of Brillouin is deduced for a tube cut off square at each end, and so for a turbulent squirt at the exit; also, the gas is assumed to flow as a liquid, without expansion within the tube, so that the kinetic energy wasted in turbulence and without pressure drop at the exit is entirely derived from pressure drop at the inlet. No account is made of the vena contracta.

It is interesting to note that Brillouin's correction, as applied by Mr. Benton, gives results which represent his experimental data much better than the correction based on stream line exit; and also that it gives for mass delivered amounts uniformly higher than experiment, and higher by amounts not to be attributed to errors of observation. This is to be expected as a consequence of reactions during expansion within the tube, and not only of vena contracta effects.

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